

Long-Term Characteristics and Trends of Benthic Oxygen and Nutrient Fluxes in the Maryland Portion of Chesapeake Bay

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ABSTRACT

Sediments began to be recognized as potentially important sites for nutrient storage, transformations and recycling in shallow ecosystems during the mid-seventies. Beginning in mid-1984, routine measurements of sediment-water nutrient fluxes were initiated at ten locations in the Maryland portion of the Bay, at both tributary and mainstem locations, for purposes of better characterizing these fluxes, estimating their impact on water quality and determining trends that develop in response to changes in nutrient loadings. Four or five sets of measurements are made annually at each station between April and November using shipboard incubation of triplicate intact sediment cores. These stations have been sampled 28 times since August 1984 and sediment data are available characterizing nutrient fluxes for several tributary and mainstem areas of the northern half of the Bay.

To place sediment nitrogen and phosphorus releases in a system-wide perspective, estimated annual fluxes were compared to external nutrient inputs (sum of diffuse, point and atmospheric sources) for selected areas of the Bay. The ratio of sediment nutrient release to external input ranged from about 0.7 to 4.1 for nitrogen and 1.3 to 7.0 for phosphorus, indicating the importance of sediments as a seasonal source of nutrients. Additionally, the relative importance of sediments as a nutrient source was inversely proportional to nutrient loading rates from external sources. These data, coupled with seasonal chlorophyll-a measurements, indicate that the spring bloom is supported by external ("new") nutrient inputs while summer and fall algal stocks are supported by recycled nutrients.

Examination of nutrient concentrations in the top 5 cm of sediments suggests that there is the equivalent of a 2 to 10 and 3 to 30 year supply (relative to external inputs) of nitrogen and phosphorus, respectively, in sediments. Further evidence suggests that the magnitude of sediment nutrient release is ultimately related to the intensity of nutrient loading from external sources. Data from the mainstem, Potomac, Patuxent, and Choptank Rivers indicate a strong, positive relationship between annual sediment flux and nutrient loading. While preliminary, these analyses suggest that substantial reductions in external nutrient inputs will result in rapidly decreasing sediment releases of nutrients.

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 biomass levels in many estuaries (including por-

tions of Chesapeake Bay) appear to be related to the magnitude of nutrient loading (Boynton *et al.*, 1982a). Excessive algal production is often sustained through the summer and fall periods by rapid recycling of essential nutrients. Sediment oxygen consumption (SOC) appears to be related to the amount of labile organic matter reaching the sediment surface and the magnitude of SOC is sufficiently high in many regions to be a major loss term in oxygen budgets (Hargrave, 1969; Kemp and Boynton, 1980).

Research conducted in Chesapeake Bay and other estuaries during the late 1970's and early 1980's indicated that estuarine sediments could act as both important storages and sources of nutrients as well as sites of intense oxygen consumption (Kemp and Boynton, 1984). For example, it was found that during summer periods in the Choptank and Patuxent estuaries, 40-70% of total oxygen utilization was associated with sediments and 25-70% of algal nitrogen demand was supplied from estuarine sediments (Boynton *et al.*, 1982b). Information of this type helped focus attention on estuarine sediments as an important component of nutrient dynamics in shallow systems and routine measurements of sediment-water exchanges of oxygen and nutrients were incorporated into the Maryland Chesapeake Bay Water Quality Monitoring Program. This program was initiated in 1984 and six years of data have now been collected.

The rationale for including sediment-water exchange measurements in the monitoring program was based on the following conceptual model relating nutrient inputs to water quality conditions. Nutrients and organic matter enter the Bay from a variety of sources, including sewage treatment plant effluents, riverine inputs, local non-point source drainage and direct rainfall on Bay waters. These nutrients ("new nutrients") are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. Much of this particulate material sinks to the bottom and is remineralized. Nutrients released from sediments ("recycled nutrients") are utilized by algal communities and again a portion of this newly produced organic matter sinks to the bottom. The continued deposition of organic matter contributes to the development of anoxic conditions, causing a loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative capacity and large nutrient storage of sediments insure a large return flux of nutrients to the water column which sustains continued phytoplankton growth. Continued growth supports deposition of

organics to deep waters which creates anoxic conditions typically associated with eutrophication of estuarine systems. 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 indicators of the effectiveness of nutrient control actions.

In this paper we provide an overview of results from this portion of the monitoring program as well as results from other concurrent studies of sediment nutrient processes. Specifically, we describe spatial and temporal patterns of sediment-water exchanges, compare sediment fluxes to external nutrient inputs and sediment nutrient storages, examine field and laboratory data for indications of the sensitivity of sediment fluxes to temperature and to changes in deposition rates and finally present trends in flux rates related to nutrient loading regimes for several areas of Chesapeake Bay.

Station Locations and Sampling Frequency

A listing of all station locations and some station characteristics are provided in Table 1. Four of the ten stations were located along the salinity gradient in the mainstem Bay between Point No Point (north of the mouth of the Potomac River) and Still Pond Neck (20 km south of the Susquehanna River mouth). Two additional stations were 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. Several earlier studies (Boynton *et al.*, 1980, 1984 and Boynton and Kemp, 1985) indicated that much of the spatial variability in sediment-water exchanges would be included in such a station array.

The sampling frequency for the Sediment Oxygen and Nutrient Exchange (SONE) program was based on seasonal patterns of sediment water exchanges observed in previous studies conducted in Chesapeake Bay (Kemp and Boynton, 1980; Kemp and Boynton, 1981; Boynton *et al.*, 1982b; and Boynton and Kemp, 1985). These studies indicated that sediment exchanges were generally positively correlated with temperature. In light of these results, four or five sets of measurements were made between April and November each year. Measurements were made more frequently (bi-weekly to monthly) during several years (1987 and 1989)

STATION NAME	LATITUDE DEG MIN	LONGITUDE DEG MIN	STATION DEPTH, m	SALINITY REGIME*
PATUXENT RIVER				
St. Leonard Creek	38°22.88'	76°30.06'	7.0	Mesohaline
Buena Vista	38°31.12'	76°39.82'	5.8	Oligohaline
CHOPTANK RIVER				
Horn Point	38°37.18'	76°08.09'	8.2	Mesohaline
Windy Hill	38°41.45'	75°58.30'	3.8	Oligohaline
POTOMAC RIVER				
Ragged Point	38°09.86'	76°35.52'	16.5	Mesohaline
Maryland Point	38°21.37'	77°11.49'	10.2	Oligohaline
CHESAPEAKE MAINSTREAM				
Point No Point	38°07.99'	76°15.13'	14.2	Mesohaline
R-64	38°33.59'	76°26.63'	16.8	Mesohaline
R-78	38°57.81'	76°23.62'	15.8	Mesohaline
Still Pond	39°20.87'	76°10.87'	10.4	Oligohaline

* Oligohaline 0.5 - 5.0 ppt, Mesohaline 5.0 - 18.0 ppt.

Table 1. Names, locations, depths, and salinity characteristics of stations routinely sampled as part of the MD Chesapeake Bay Water Quality Monitoring Program. Station locations are also shown in Figure 1.

at a few stations in the mainstem bay. During the spring of 1990 many cores were collected at a mid-bay site (R-64) for use in laboratory experiments.

DATA COLLECTION

Water Column Profiles

At each station vertical water column profiles of temperature, salinity and dissolved oxygen were obtained at 2 m intervals from the surface to the bottom immediately prior to obtaining intact sediment cores for incubation. The turbidity of the water was measured using a Secchi disc. Near-surface (approximately 0.5m) and near-bottom (approximately 1m from the bottom) water samples were also collected using a high volume submersible pump system. Samples were filtered using 0.7 μm GF/F filter pads, and immediately frozen. Samples were analyzed for the following dissolved nutrients: ammonium (NH_4), nitrite

(NO_2), nitrite plus nitrate ($\text{NO}_2 + \text{NO}_3$) dissolved inorganic phosphorus (DIP or PO_4) and silicic acid ($\text{Si}(\text{OH})_4$).

Routine Sediment Core Collection and Incubation

Intact sediment cores were obtained at each station using a modified Bouma box corer. After deployment and retrieval of the box corer, the metal box was removed to reveal the Plexiglas liner containing the sediment core. The core was visually inspected for disturbance. A satisfactory core was placed in a darkened, water-filled holding incubator prior to further processing. Three intact cores were used to estimate net exchanges of oxygen and dissolved nutrients between sediments and overlying waters (Figure 2). Prior to beginning flux measurements, the overlying water in the core was replaced by fresh bottom water to insure that water

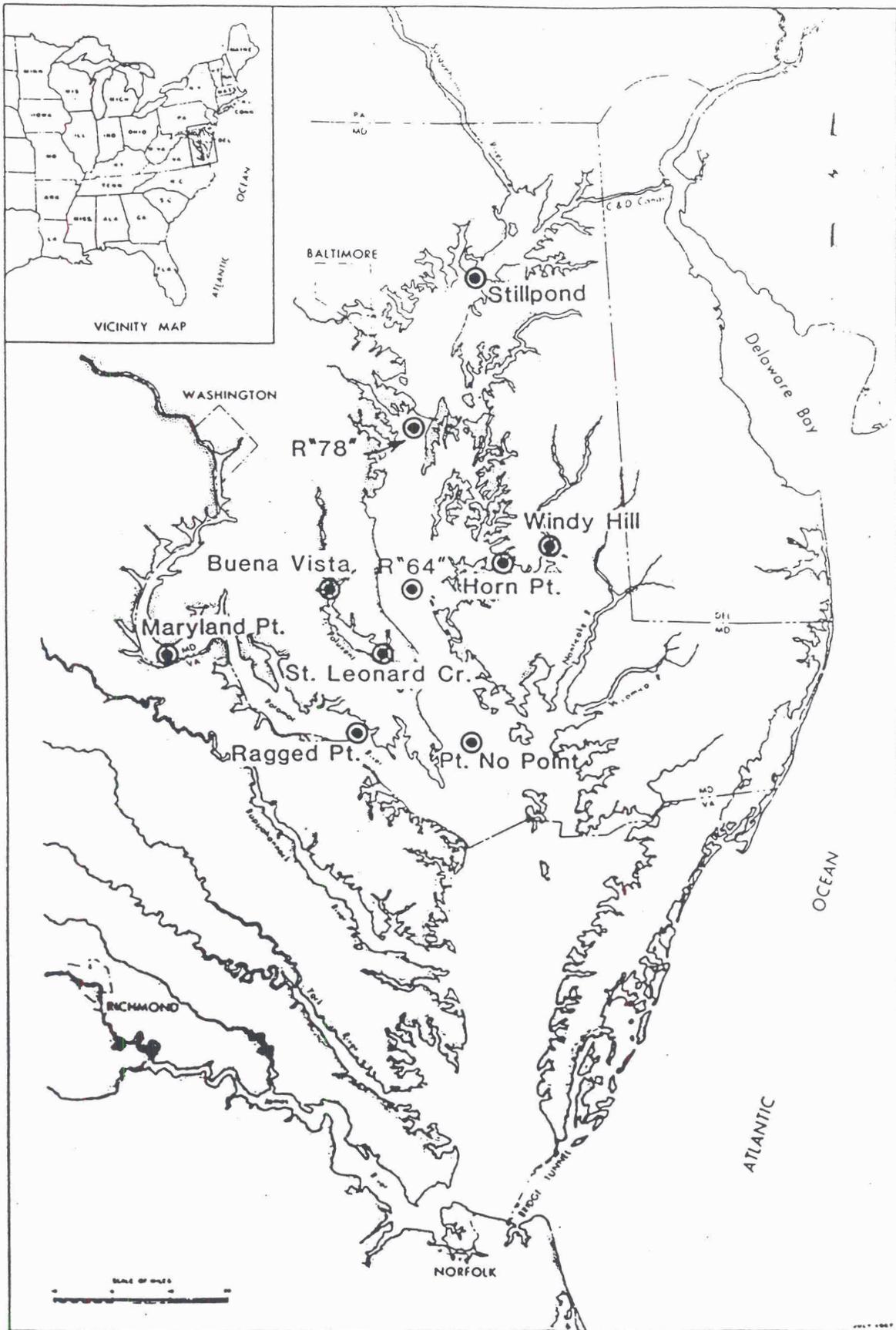


Figure 1. Location of sediment oxygen and nutrient exchange (SONE) stations in the Maryland portion of the Chesapeake Bay.

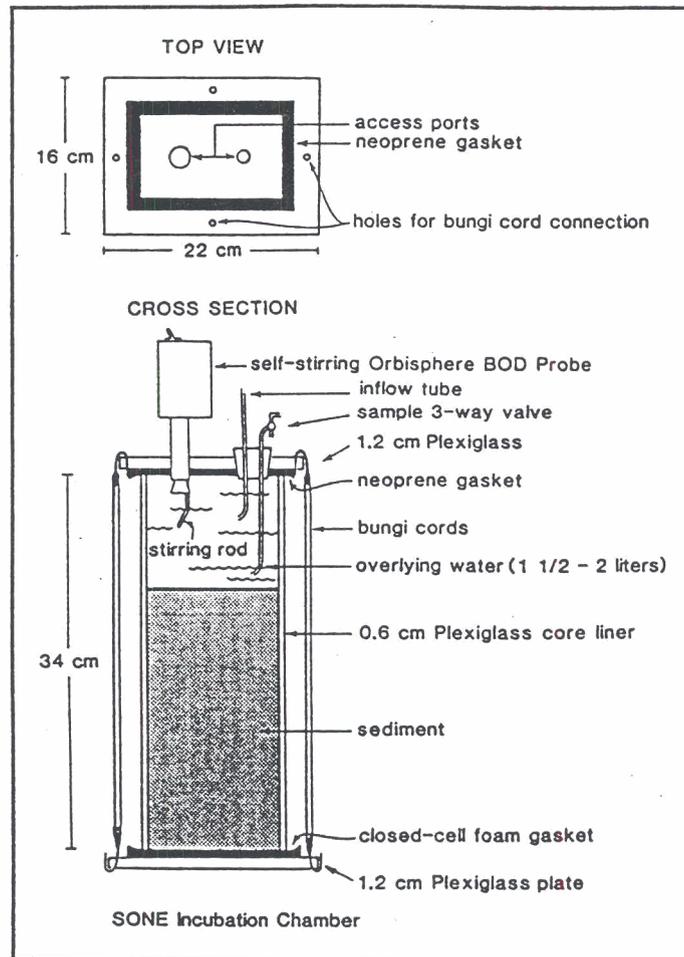


Figure 2. Schematic diagram of the incubation chamber used in making SONE measurements.

quality conditions in the core closely approximated in-situ conditions. Gentle circulation of water, with no induction of sediment resuspension, was maintained in the cores during the measurement period via the stirring devices attached to the O_2 probes. The cores were placed in a water bath to maintain ambient temperature. The cores were also kept in the dark to stop photosynthetic processes. Oxygen concentrations were recorded and overlying water samples (35 ml) extracted from each core every 30 or 60 minutes (depending on the rate of oxygen uptake) over a 2-5 hour incubation period. During the incubation period, five overlying water samples were extracted from each core. As a nutrient sample was extracted from a core, an equal amount of ambient bottom water was added. An opaque Plexiglas liner filled with bottom water, incubated and sampled as described above served as a blank. Overlying water samples were filtered and immediately frozen for later analysis for ammonium (NH_4), nitrite

(NO_2), nitrite plus nitrate ($NO_2 + NO_3$), dissolved inorganic phosphorous (DIP or PO_4) and silicious acid ($Si(OH)_4$) concentrations. Oxygen and nutrient fluxes were 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.

Special Studies

During the early spring of 1990 intact sediment cores were collected from station R-64 in the mesohaline portion of the mainstem bay for use in two laboratory experiments. The purpose of both experiments was to determine the response of sediment fluxes to sharply decreased inputs of fresh organic matter under both aerobic and anaerobic conditions. In the first experiment three cores were maintained at ambient conditions (in darkness at $15^\circ C$, dissolved oxygen in overlying water near saturation) for a period of 45 days. A total of eight flux measurements were made dur-

ing this period using the methods described above. During periods between flux measurements water overlying sediments in the cores was continually replaced with filtered, ambient water to remove most particulate organic materials.

In the second experiment a set of intact sediment cores were also held under both aerobic and anaerobic conditions (18 C) and continually flushed with filtered water. Sub-cores were taken after 1, 2.5 and 4.5 weeks after collection and sectioned into discrete depth intervals (0.0-0.5, 0.5-1.0, 1.0-2.0, 2.0-3.0, 3.0-4.0 and 4.0-5.0 cm). Approximately 6ml of sediment was placed in 14ml serum bottles under anaerobic conditions and incubated for 1-2 weeks. Concentrations of SO_4 were determined in initial and final serum bottles and then converted to fluxes for specific sediment depth intervals.

Chemical Analyses

Detailed reference material pertaining to all chemical analyses used in this study is given in Boynton and Rohland (1990). In brief, methods for the determinations of dissolved nutrients were as follows: ammonium (NH_4), nitrite (NO_2), nitrite plus nitrate (NO_2+NO_3), and dissolved inorganic phosphorus (DIP or PO_4) were measured using the automated method of EPA (1979); silicic acid ($Si(OH)_4$) was determined using the Technicon Industrial System (1977) method. Concentrations of sulfate (SO_4) were determined using ion chromatography.

RESULTS AND DISCUSSION

Spatial patterns of sediment oxygen consumption (SOC) and nutrient fluxes

Some broad spatial patterns of sediment-water exchanges of oxygen and nutrients have been developed by combining flux rates for similar stations and averaging all measurements available between April 1985 and October 1990 ("location averaged fluxes"). The relatively large error bars evident in Figure 3 result primarily from the strong seasonal nature of sediment-water fluxes rather than from variability associated with replicate measurements.

Location averaged SOC rates ranged between 0.70 and 1.35 $g\ O_2\ m^{-2}\ d^{-1}$ (Fig.3). These rates are moderate to large when compared with SOC rates reported for other temperate estuaries (Nixon 1981). It is important to note that most of our flux measurements were made during the warm portions of the year (April-November). Comparisons of our data with other seasonally or annually

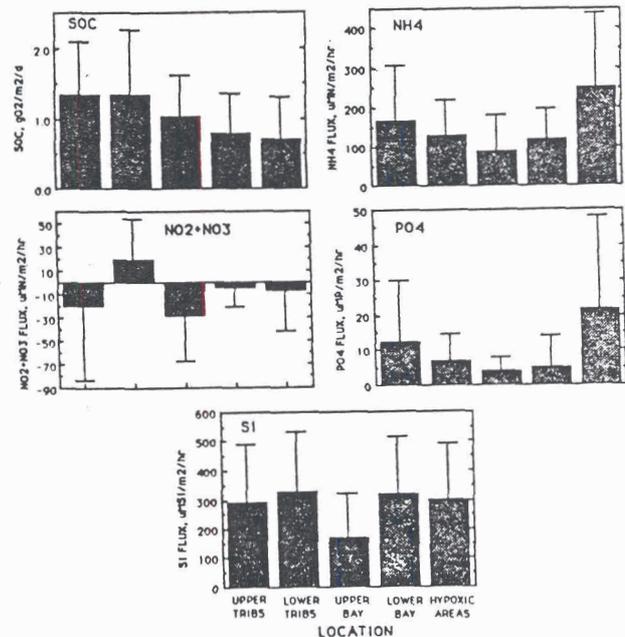


Figure 3. Average sediment-water fluxes (mean and standard deviation) for several zones of the Maryland portion of Chesapeake Bay. Zones included the following station groupings (see Figure 1): Upper tributaries = Buena Vista, Windy Hill and Maryland Point; Lower tributaries = St. Leonard Creek and Horn Point; Upper Bay = Still Pond; Lower Bay = Point No Point; Hypoxic Areas = R-64, R-78 and Ragged Point. Means are based on all data collected between April, 1985 and October, 1989.

averaged flux data, which may include winter measurements, should be done cautiously. During the winter of 1988-89 we were able to make a number of measurements and it is now clear that SOC is low, as are nutrient fluxes in the mainstem Bay, when temperatures are below 10°C (Garber et al., 1989). SOC tended to be highest at the shallow tributary stations and lower in the deeper mainstem bay. Stations could be separated into three groups: high average SOC's were found in the Patuxent and Choptank Rivers; rates were intermediate at the upper bay station and considerably lower in the Potomac River and mid-mainstem bay. Caution must be exercised in utilizing SOC rates as a general indicator of sediment metabolism. Difficulties arise in areas where dissolved oxygen concentrations are reduced (*i.e.*, $< 2\text{mg}\ l^{-1}$). In those situations SOC appears to reflect ambient dissolved oxygen conditions rather than sediment metabolism. The lower average SOC rates observed in the lower bay and in hypoxic

areas are indicative of chronic low oxygen conditions in overlying waters rather than low rates of sediment metabolism. At the remaining three areas (upper bay and upper and lower tributaries) low oxygen conditions are rare, and SOC is a reasonable index of sediment metabolism. We speculate that the differences between tributary and upper bay sites is primarily regulated by the quality of organic matter reaching the sediment surface. The quality is higher in the tributaries where phytoplanktonic debris dominates and lower in the upper bay where refractory terrestrial detritus is important (Boynton and Kemp, 1985).

The results of inorganic nitrogen flux measurements reported here are consistent with earlier studies in Chesapeake Bay (Boynton *et al.*, 1980) and elsewhere (Nixon *et al.*, 1976, Hammond *et al.*, 1985, Zeitzschel, 1980) which indicated that NH_4 dominates benthic fluxes in productive temperate estuaries (Fig. 3). The release of NH_4 from sediments was generally many times greater than the net exchange of nitrate + nitrite. At most stations NH_4 flux accounted for 70-100% of the total DIN flux (the sum of NH_4 plus nitrate + nitrite) from the sediment. Location averaged fluxes of NH_4 ranged from $89 \mu\text{MN m}^{-2}\text{hr}^{-1}$ in the upper bay to $258 \mu\text{MN m}^{-2}\text{hr}^{-1}$ in areas experiencing hypoxia or anoxia. The average flux at most stations fell between $100\text{-}200 \mu\text{MN m}^{-2} \text{hr}^{-1}$. The factors responsible for these spatial differences are probably related to several environmental variables, the most important being the redox state of the sediments and overlying water and the rate of deposition of particulate organic nitrogen. High fluxes in hypoxic areas would be expected, because 1) there is typically a large supply of organic matter to the sediment surface in these areas to fuel ammonification, and 2) hypoxic conditions would prevent the transformation of ammonium to NO_3 and subsequently to N_2 gas via denitrification. Lower ammonium fluxes might be expected in the lower and upper bay because deposition rates are lower in the former and of low quality in the latter, and nitrification of some fraction of the ammonium produced takes place at both sites, at least in the spring and fall (Twilley and Kemp, 1987). Overall, the magnitude of "location averaged" ammonium fluxes is as follows: hypoxic areas > upper tributaries > lower tributaries > lower bay > upper bay .

Fluxes of $\text{NO}_2 + \text{NO}_3$ followed pronounced spatial patterns which included shifts in direction of the fluxes across the sediment-water interface (Fig. 3). Lower tributary stations in the Patuxent and Choptank were characterized by release of $\text{NO}_2 +$

NO_3 from the sediment to the water at rates that averaged around $20 \mu\text{MN m}^{-2}\text{hr}^{-1}$. Highest rates of sediment uptake generally occurred at upper tributary stations that were characterized by high levels of dissolved nitrate in the water overlying sediments. The net releases of $\text{NO}_2 + \text{NO}_3$ observed in lower tributaries reflect predominantly oxidized environments both in surficial sediments and overlying waters. Such conditions favor sediment-associated nitrification, hence the net release of nitrate from the sediments. At other locations in the bay, the redox environment appears to shift between oxic and anoxic conditions, the former favoring nitrification, the latter favoring nitrate metabolism and denitrification. Nitrate formation and consumption appear at times to be in balance resulting in no net flux across 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 net removal of $\text{NO}_2 + \text{NO}_3$ from overlying waters is small. At these stations ammonium regeneration appears to be the only significant route of nitrogen remineralization occurring in the sediments other than burial in the accreting sediment column.

Fluxes of dissolved inorganic phosphorus ranged from about $3.0 \mu\text{MP m}^{-2}\text{hr}^{-1}$ in the upper bay to $22 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at locations exposed to hypoxic conditions (Fig. 3). Stations could also be separated into two large groups based on average DIP fluxes: one group consists of the lower tributary stations in the Patuxent and Choptank and the lower and upper mainstem Bay where fluxes were less than $7 \mu\text{MP m}^{-2} \text{hr}^{-1}$. The second group consists of the upper tributary stations and hypoxic areas where average station fluxes were in excess of $12 \mu\text{MP m}^{-2} \text{hr}^{-1}$. These results suggest that relatively high DIP fluxes occur in the low salinity reaches of some tributaries as well as the regions that experience hypoxic conditions. Finding the mechanisms that seem to "turn on" and "turn off" DIP fluxes is clearly crucial to understanding phosphorus dynamics at the sediment-water interface. We have shown that the redox condition of sediments and overlying waters is one such important factor, particularly in the mainstem bay (Boynton *et al.* 1989). However, the DIP flux data collected to date suggest that the mechanisms regulating DIP fluxes probably differ at various locations within the bay. For example, DIP fluxes tended to be highest along the deeper reaches of the mainstem bay and the upper tributaries. The release of DIP from sediments along the deep mainstem bay is most likely associated with low redox potential that accompanies the depletion of

oxygen in the overlying water. Such release of DIP from sediments during anoxic conditions is a well known process in lakes and fjords and involves the redox-driven dissolution of iron phosphates and other compounds (Krom and Berner, 1980 and Klump and Martens, 1981). It seems unlikely that a similar mechanism controls the relatively large fluxes of DIP from sediments in the upper tributaries, because overlying waters in these regions are always well-oxygenated. It seems probable that substantial PO_4 fluxes in upper tributaries result from infaunal irrigation of sediments by the substantial benthic communities present at these sites (Holland, 1989).

Location-averaged Si fluxes for all stations were always from sediments to the water and were on the order of $150-400 \mu M Si m^{-2} hr^{-1}$ (Fig. 3). High fluxes occurred along the deep mainstem bay and in the tributaries, and low fluxes were observed in the upper mainstem bay areas. Silicate fluxes among major regions appeared to increase in parallel with increasing salinity: Upper Bay < Upper Tributaries < Lower Tributaries < Hypoxic Areas. This pattern is consistent with a conceptual model which would predict increasing silicate cycling in higher salinity regimes (Yamada and D'Elia, 1984) in parallel with the increasingly important role of diatom production in the phytoplankton communities along the estuarine salinity gradient.

Temporal patterns of SOC, NH_4 and PO_4 Fluxes

Most stations exhibited clear seasonality in SOC in which the highest rates occurred in May or June with a lesser peak often observed in fall (Fig.4). An intriguing feature of this pattern is that it is out of phase with the temperature cycle by 2-3 months. This pattern probably results because macrofaunal oxygen consumption and oxygen consumption by nitrifying bacteria are high in spring and decrease later in summer and because during spring there is an abundant supply of labile organic matter available from deposition of the spring diatom bloom. Additionally, at stations subject to periodic anoxia (e.g. R-64, Ragged Point) seasonal patterns of SOC were strongly influenced by the timing and duration of low-oxygen conditions which were responsible for the generally low rates in summer (Fig. 4). It appears that fall increases in SOC resulted from reoxygenation of bottom waters and subsequent oxidation of fall bloom organic matter and the oxidation of reduced sulfur compounds created during the summer period (Roden 1990).

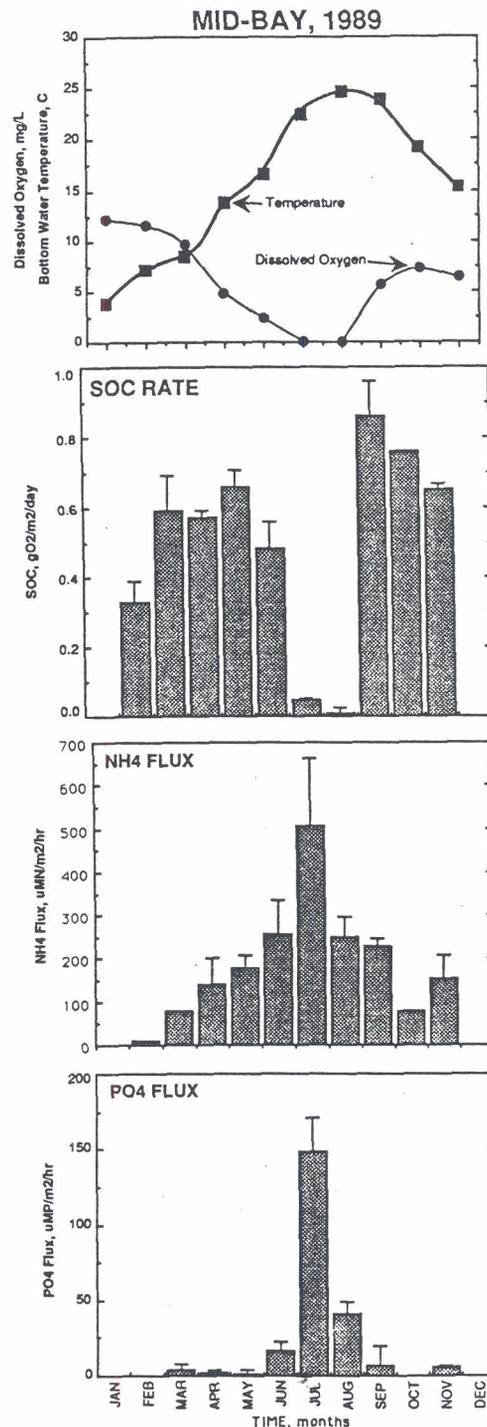


Figure 4. Bottom water temperature and dissolved oxygen concentration and net sediment-water exchanges (mean and standard deviation) of oxygen, ammonium and phosphate. Measurements were made monthly during 1989 at a station in the mesohaline region of the mainstem bay (STA. R-64).

Ammonium fluxes also exhibited distinct seasonal patterns with maximum rates of sediment release occurring in summer in most cases, but generally prior to the annual temperature maximum. An example of a typical annual cycle for NH_4 fluxes is shown in Figure 4 for a station in the mesohaline portion of the mainstem bay. Exceptions to this pattern were observed in the upper bay (Still Pond Station) where no seasonal pattern could be discerned and fluxes were generally small ($< 200 \mu\text{MN m}^2 \text{hr}^{-1}$). Fluxes of NH_4 may be relatively small in the spring because some NH_4 is lost to sediment nitrification and some particulate nitrogen is incorporated into macrofaunal biomass. In early summer ammonium fluxes increase as nitrification decreases, macrofaunal stocks decline and temperature exerts a strong influence on bacterial metabolism.

Seasonal variations in DIP fluxes were also quite consistent among stations. All but two sites followed a simple unimodal cycle with periods of maximum sediment release occurring during the warm periods of the year, but again generally preceding the annual temperature maximum (Fig. 4). Along the mainstem bay, DIP fluxes were generally low in spring and fall, with highest fluxes from the sediment to the overlying water occurring in June-August. This pattern is consistent with the view that large sediment-water exchanges of PO_4 are associated with low oxygen in overlying waters and sediments occurring in summer (Fig. 4).

To examine the influence of temperature on sediment-water exchanges, fluxes were plotted as a function of temperature. For most nutrients (excluding $\text{NO}_3 + \text{NO}_2$) at most locations there was an indication of increased fluxes at higher temperatures. An example is shown in Figure 5 where Si and NH_4 fluxes are plotted against temperature for stations in the lower Patuxent River and lower Potomac Rivers, respectively. In both cases there was a strong positive relationship between flux and temperature, but only for data collected prior to August when seasonal temperatures normally reach maximum levels. Flux data at these and other stations typically diverge strongly at this time of year from the pattern expected based on temperature influences alone. This suggests that some factor other than temperature is involved in regulating late summer fluxes. We will present data later which suggests that fluxes are regulated by the availability of labile organic matter. In the lower panel of Figure 5 fluxes collected in 1986 appear to respond to temperature much as in other years but the magnitude of fluxes was consider-

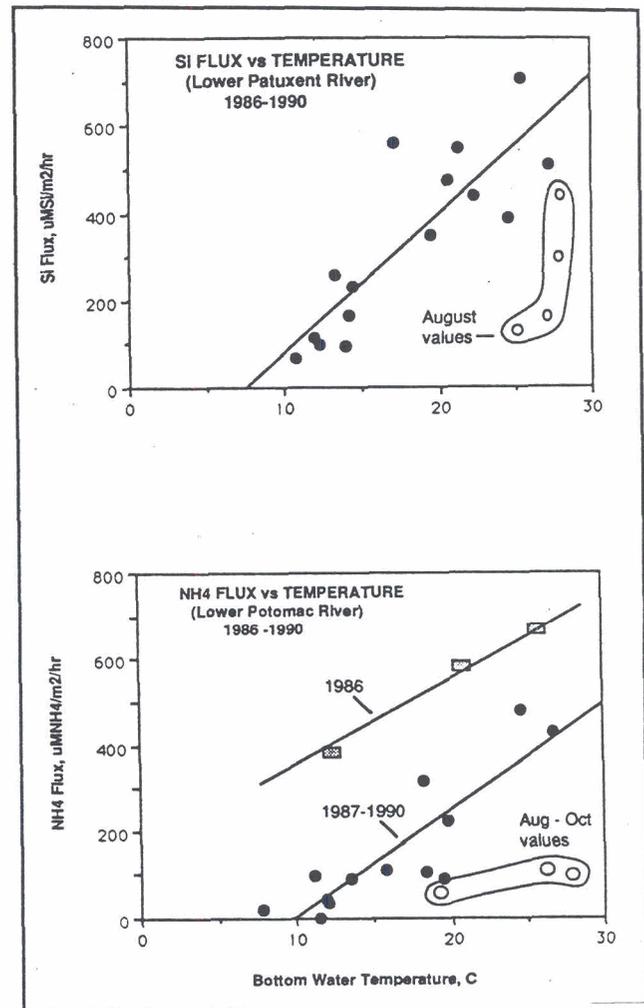


Figure 5. Scatter plots of bottom water temperature vs net sediment-water exchanges of silicate (Si) and ammonium (NH_4) from several lower tributary river stations (see Figure 1). Data indicated with open circles were not included in calculating linear regression lines. Each flux measurement is the mean of triplicate samples.

ably higher. It so happens that nutrient loading to the Potomac was particularly high in the last months of 1985 and the first months of 1986. The conceptual model presented earlier suggests that high nutrient loading would lead to high algal production and biomass and eventually to higher deposition rates of labile organic matter to the sediment surface. The higher fluxes observed in 1986 are consistent with this explanation.

Sediment-Water Fluxes Relative to Inputs of "New Nutrients"

To provide some ecosystem level perspective concerning the possible importance of sediment-water nutrient exchanges we have compared estimated

annual rates of nitrogen and phosphorus releases from sediments to annual inputs of nitrogen and phosphorus from all sources for four regions of the bay (Table 2). In part, this is a comparison of the relative importance of "new nutrients" to "recycled nutrients" in the sense of Dugdale and Goering (1967). Nutrient input data were collected and organized by Summers et al. (1989) and included total nitrogen and total phosphorus from municipal and industrial point sources, diffuse source loadings and atmospheric deposition (wet fall only) directly to surface waters. Estimates of annual benthic fluxes were developed from data collected in the monitoring program and represent average annual fluxes for the years 1985 and 1986, as is the case for nutrient loads. We use the term annual sediment fluxes for convenience but these represent average fluxes for the period April - November of each year.

The magnitude of these two sources is shown in Table 2 along with the ratio of sediment nutrient flux to inputs of new nutrients. The flux : input ratio for nitrogen ranged from 0.72 in the Potomac to 4.28 in the Choptank River and generally indicated that nitrogen recycled from sediments was as large or considerably larger term than inputs of new nutrients. The phosphorus ratio followed the same pattern but phosphorus recycled from sediments was a much larger term than inputs of new phosphorus.

While the sediment terms are large, particularly for phosphorus, relative to inputs of new nutrients, both are obviously important in sustaining primary production in overlying waters. It appears that the spring diatom bloom is largely supported by new nutrients while summer and fall production is supported by recycled nutrients, some portion of which comes from sediments (Malone et al. 1984). Thus, there is a 3-4 month separation in time between when new nutrients dominate (March-May) and when recycled nutrients are the major source (June-September). This time delay implies some seasonal retention of nutrients within the system and it appears that the sinking of the spring bloom to the sediments when temperatures are still low (<10 C) is a primary retention mechanism. This also suggests that the magnitude of sediment-water fluxes, which are largest in summer, is ultimately set by the magnitude of the spring bloom deposition event which in turn is related to nutrient inputs from the land and atmosphere.

Finally, it appears that the relative importance of "new" versus "recycled" nutrients varies inversely according to the degree of nutrient loading to which a particular estuary is exposed. Data were available to examine the nature of this relationship for four sites in the Chesapeake system (Fig.6). While we have a very limited number of sites, the data suggest rapidly increasing importance for recycled nutrients at "new nutrient"

LOCATION	ESTUARINE AREA ^a (m ² x 10 ⁶)	AVERAGE SEDIMENT FLUX ^b (uM N or P/m ² /hr)		ANNUAL SEDIMENT FLUX (Kg x 10 ⁶ N or P/yr)		TOTAL ANNUAL INPUTS ^d (Kg x 10 ⁶ N or P/yr)		FLUX / INPUT RATIO		
		N	P	N	P	N	P	N	P	
MARYLAND MAINSTEM BAY										
upper ^c	1167	54	3.8	7.73	1.20					
lower ^c	2703	190	15.2	62.98	11.19	80.52	3.75	0.88	3.30	
POTOMAC RIVER										
upper	206	147	2.2	3.71	0.12					
lower	748	238	17.8	21.83	3.62	35.36	2.92	0.72	1.28	
PATUXENT RIVER										
upper	25	189	17.3	0.58	0.12					
lower	111	128	6.1	1.74	0.18	1.73	0.20	1.34	1.50	
CHOPTANK RIVER										
upper	15	148	17.3	0.27	0.07					
lower	285	170	7.7	5.94	0.60	1.45	0.11	4.28	6.09	

^a Areas of all estuarine segments are from Cronin and Pritchard (1975).

^b Benthic nutrient flux data are from Boynton et al. (1990).

^c Upper and lower portions of study sites refer to areas upstream and downstream of the turbidity maximum zone, respectively.

^d Nutrient input data from Summers et al. 1989

Table 2. Summary of estimated annual rates of sediment nutrient releases (NH₄ + NO₃ and PO₄) and annual total N and P inputs for selected areas of Chesapeake Bay.

loading rates of less than $10\text{gN m}^{-2}\text{yr}^{-1}$ and $1\text{gP m}^{-2}\text{yr}^{-1}$. The sharp increase in the relative importance of recycled nutrients under low nutrient loading conditions may in part explain the relatively small differences observed in phytoplankton production among these systems (Sellner et al. 1989). The small number of sites included in this analysis makes the results quite speculative. It would obviously be useful to attempt to add additional sites which are both more and less heavily loaded to see if this relationship persists.

The "Memory" of Sediment Nutrient Processes

It is commonly assumed that sediments represent the only important, long-term (>1 year) storage site for such materials as nutrients and toxics in many estuarine systems. This makes good intuitive sense because the water residence time of the mainstem bay and tributary rivers of the Chesapeake are far less than one year (Bouicourt, pers comm) and hence there is little possibility for long-term storage in the water. Further, the mass of nutrient material stored in living biota may be substantial at some times of the year (Holland et al 1989), but does not appear to accumulate from one year to the next. Annual nutrient budgets developed for four regions of the Chesapeake also suggest sediments as the single most important storage. For example, in the Potomac River, approximately 87% of the total nitrogen in the system is contained in the top 5 cm of the sediment column. These calculations are sensitive to the depth of the sediment column used. We chose 5 cm because nutrient concentrations were generally constant below this depth suggesting this to be the depth to which sediments are actively connected to water column processes. Almost 91% of the total phosphorus is partitioned into sediments, with 8% and 2% associated with water column materials and biota and benthic infauna, respectively. Other portions of the bay exhibit similar patterns (Boynton et al. 1991).

We can also compare the relative magnitude of sediment nutrient storages to inputs of new nutrients. Some sediment characteristics and total annual inputs of new nutrients for four regions of the bay are summarized in Table 3. The *stock : input* ratio indicates that stocks range from 1.3 to 10.8 and 3.0 to 27.8 times larger than annual inputs for nitrogen and phosphorus, respectively, for several regions of the bay. This ratio would be smaller if only a single year's worth of deposited material was considered as stored material. In fact, the material accumulated in 5 cm of the sediment column represents between 5 and 20 years of deposition, depending on location in the bay

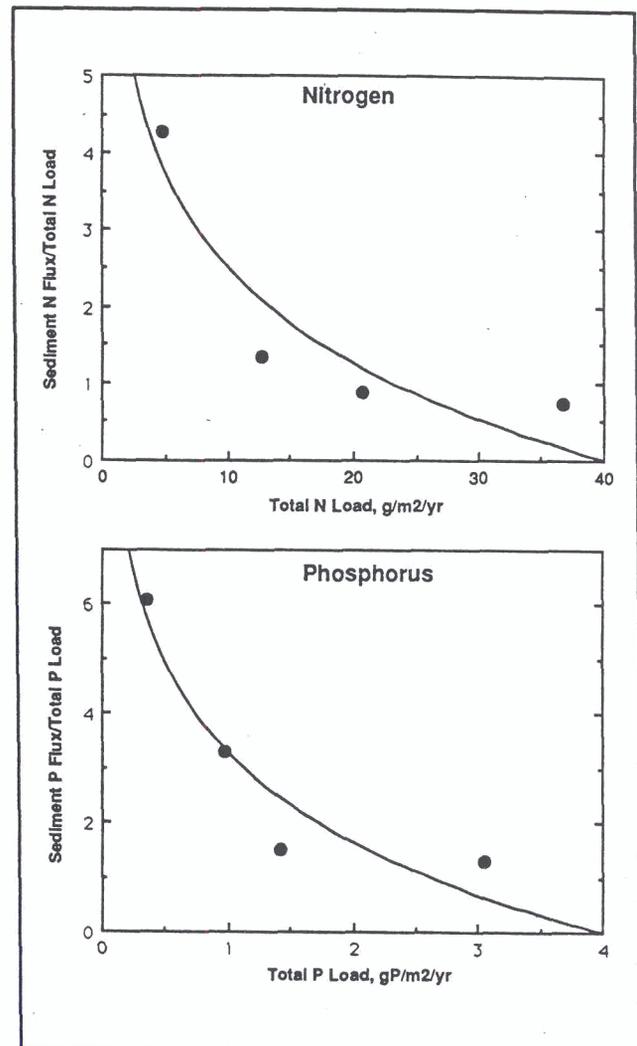


Figure 6. Scatter plots of total nitrogen and phosphorous loading versus the ration of net sediment-water fluxes of NH_4 and PO_4 to loads of total nitrogen and phosphorous loading. The solid lines are intended to emphasize the general shape of the relationship but are not statistical best-fit lines. Sediment-water exchange data (annual average values) are from the mid-bay region (Sta.R-64), lower Potomac (Ragged Point), lower Patuxent (St. Leonard Creek) and lower Choptank (Horn Point). Total nitrogen and phosphorous loading rates for each of these systems are from Summers et al (1989).

(Boynton et al 1991). However, nutrient concentrations in at least the top 5 cm of the sediment column decrease with depth indicating that these nutrients are still actively coupled to processes nearer the surface and in overlying waters via sediment resuspension and burrowing activities of benthic infauna. Hence, it is appropriate to include

all or some fraction of this material in an "active" storage category. Both the partitioning of nutrients and the mass of nutrients in sediments indicates that sediments are a major nutrient reservoir that could overshadow the effects of decreased inputs of "new nutrients". This type of evaluation suggests that the nutrient memory of sediments is both long and large.

However, recently collected field observations and laboratory experiments suggest the opposite is more generally the case. It appears that nutrient fluxes from sediments to overlying waters are closely coupled in time to deposition rates of labile organic matter and that nutrients buried in sediments are, for the most part, not readily recycled. These data indicate that the memory is short, probably on the order of months to a few years at most. Evidence supporting this conclusion is shown in Figure 7. Fluxes of NH_4 measured at a location in the mesohaline mainstem bay (Sta R-64) are plotted against temperature at the time of measurement (Fig. 7a). Sediment releases of ammonium reached a peak in July, prior to the annual temperature maximum, and decreased substantially in August and September. We suggest that lower fluxes result, even at higher temperatures, because labile organic matter derived mainly from deposition of the spring bloom had been exhausted. Fluxes in August and September were lower, but still substantial, and it seems likely that they were supported by material derived from summer algal blooms. Alternative explanations for this pattern are possible but do not seem reasonable. For example, nitrogen is not being temporarily sequestered in benthic biomass (and hence reducing the amount of nitrogen available for release as NH_4) because infaunal biomass levels are very low during this time of year (Holland et al 1989). Nor does it appear that nitrogen is being routed through the nitrification pathway because of hypoxic conditions of sediments. Finally, particulate nitrogen concentrations in the top 2-3 mm of sediments began to decrease after deposition of the spring bloom in late spring. Similar, but less dramatic, patterns have been reported for Aarhus Bight, an embayment in Denmark (Hjorth et al 1990) and interpreted in a similar fashion.

Laboratory experiments also indicate a close temporal coupling between fluxes and availability of labile organic matter (Fig. 7B and 7C). Both SOC (an index of aerobic metabolism) and sulfate reduction (an index of anaerobic metabolism) decreased sharply in intact sediment microcosms held under laboratory conditions of constant temperature (18 C) and no additions of

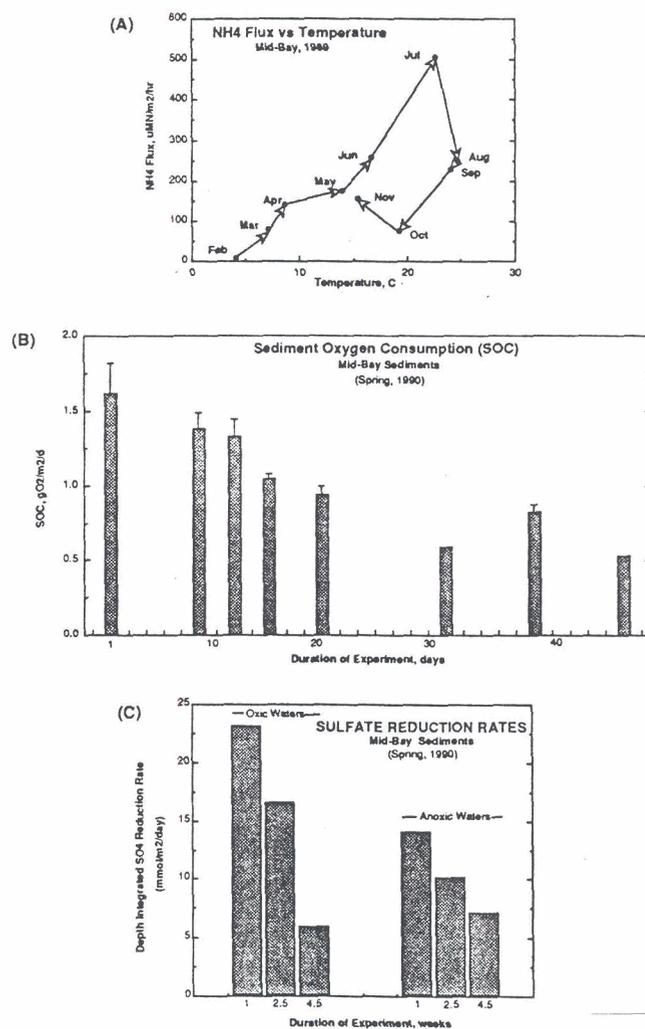


Figure 7. Three different views of the temporal behavior of sediment processes. (A) Line plot of monthly bottom water temperature versus monthly net sediment-water exchanges of NH_4 at a mid-bay station (Sta.R-64) during 1989, (B) Temporal pattern of sediment oxygen consumption rates measured in intact sediment cores collected from a mid-bay site (Sta.R-64) and maintained for 45 days under laboratory conditions of low organic matter input and aerated overlying water at 16-19 C, (C) temporal patterns of sulfate reduction rates measured in sub-cores taken from the same site as in (B). Half of the sub-cores were taken from cores which were maintained with aerated overlying water and half from cores maintained under anoxic conditions.

labile particulate organic matter to the water overlying the cores. Similar responses based on microcosm studies have been reported by Kelly and Nixon (1984) and Boynton (1985). These data suggest that at least in the middle reaches of the mainstem bay, sediment recycling of new nutrients would rapidly decrease (months to years) with decreased annual nutrient loadings.

Nutrient loading and sediment-water nutrient exchanges

Earlier we outlined a conceptual model wherein nutrient loading from all sources ultimately regulates phytoplankton production and biomass. This, in turn, influences organic matter deposition rates which sets the upper bounds for sediment-water nutrient releases. At this stage we have not investigated all the potential for linkages implied by this model but have started to search for relationships between nutrient sources (i.e. loading rates) and benthic nutrient releases. We have chosen to start with these because reduction in "new nutrient" inputs is a primary management objective and benthic nutrient fluxes should be related to inputs and are largely responsible for stimulating summer algal blooms which exacerbate poor water quality conditions.

In general it appears that sediment releases of ammonium and phosphate are related to nutrient inputs as we have shown in some earlier, more preliminary analyses (Boynton et al 1989). As an example, there appears to be a moderately strong relationship between annual average river flow (used here as a surrogate variable for nutrient loading) and summer ammonium fluxes at a station in the lower Patuxent River (St. Leonard Creek). While there is considerable scatter, there is a factor of about 1.5 in the NH_4 flux over the range of river flows observed between 1985 and 1990 (Fig.8).

One of the problems in attempting to determine relationships such as these for a single site is that the total range in the hypothesized "causative" variable (river flow in this case) is usually quite small and, because of this, the response range (flux in this case) might also be expected to be relatively small. As a result, we try to find a small signal emerging from a system where there are clearly other factors influencing fluxes. The message is difficult to read. An alternative approach is to include both loading and flux data from several sites that encompass a larger range in nutrient loading and, presumably, sediment flux responses. The results of one such analysis are shown in Figure 9 where summer NH_4 and PO_4 fluxes were

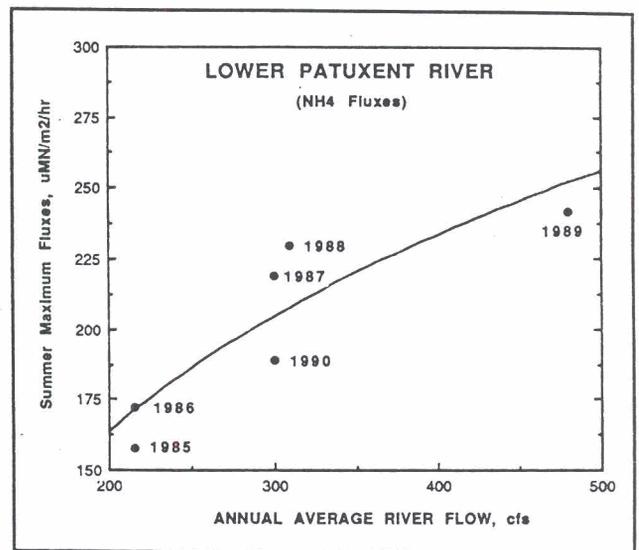


Figure 8. Scatter plot of annual average river flow versus summer maximum NH_4 fluxes at a station in the lower Patuxent River (Sta. St Leonard Creek). The solid line is intended to emphasize the general pattern but is not a statistical best-fit line.

plotted as a function of total annual nitrogen loading. While we have limited spatial coverage of sediment fluxes (1 station in the upper and lower portions of each sub-system), load-flux relationships were very strong with r^2 values of 0.73 and 0.88 for NH_4 and PO_4 , respectively. In this case the ranges in both loading and flux were considerably greater than in the earlier example based on data from just the Patuxent River.

Several additional points can also be made. First, the data collected from the lower Choptank River seem to diverge from other data, with Choptank River fluxes being relatively higher than expected for a given level of nutrient loading. This discrepancy may be more apparent than real. Results based on nutrient budget calculations indicate that the lower Choptank receives substantial nutrient additions from the mainstem bay (Boynton et al 1991). If this is the case, nutrient loading to the Choptank is higher than shown in Figure 9 and would have the effect of moving Choptank River fluxes more in line with those of other systems.

Second, there are some data points that tend to diverge from the general trend, an example of which are the fluxes measured in the lower Potomac in the summer of 1985. In this case there was but a single set of summer measurements made in August. In this case it may be that the highest fluxes occurred earlier in the summer (see Fig.4) and we have underestimated the warm season flux. This points to the need for intense sampling

through the warm period of the year in order to develop good warm season flux estimates.

Third, the load-flux relationship for ammonium indicates that for every unit reduction in load there would be roughly an equivalent reduction in sediment releases. This means that the effective load of nitrogen made available to phytoplankton would decrease by about a factor of two for every unit decrease in loading from external sources.

Finally, we found a stronger relationship between nitrogen loading and PO₄ release than between phosphorus loading and PO₄ release. This seems counterintuitive at best and impossible at the extreme. A tentative explanation which is consistent with some field and experimental results (D'Elia et al 1986) is that phytoplankton production and algal stocks are largely controlled by nitrogen availability in some portions of these systems. If that is the case, then deposition of organic matter to the sediments, and resultant sediment fluxes, would be more related to nitrogen than phosphorus loading.

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

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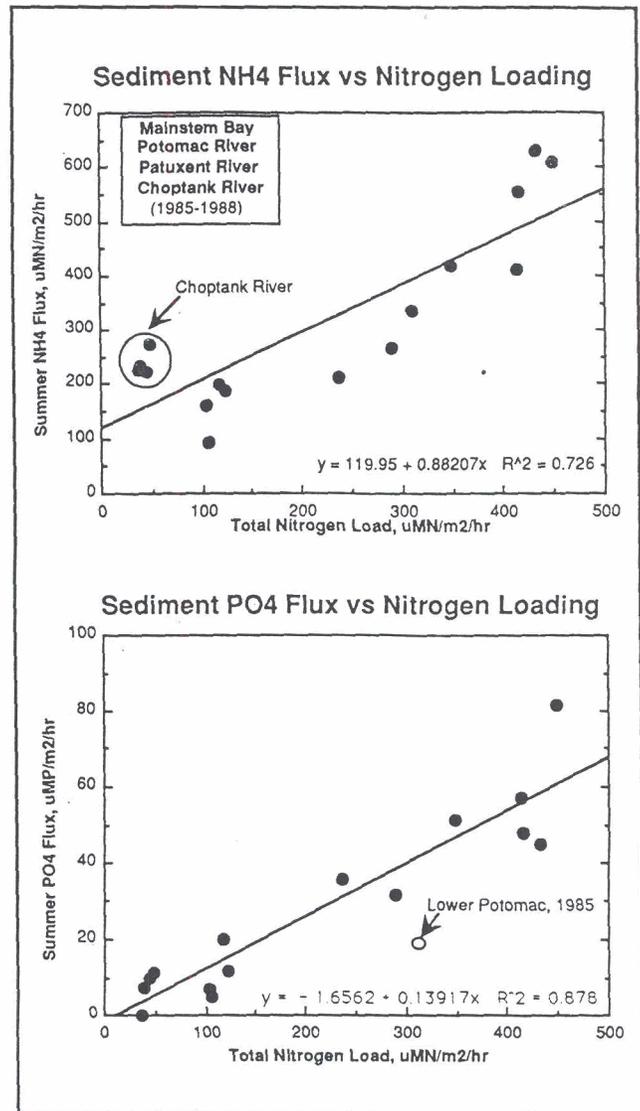


Figure 9. Regression plot of total annual nitrogen and phosphorus loading versus summer NH₄ and PO₄ fluxes at four locations in the Maryland portion of the bay for the years 1985-1988. Station locations are as in Figure 6. Nitrogen and phosphorus loading data are from Summers et al (1989). The bold solid lines are based on linear best-fit models. The data point plotted as an open circle was not included in these calculations.

- Boynton, W.R., W.M. Kemp and C.W. Keefe. 1982a. A comparative analysis of nutrients and other factors influencing estuarine phytoplankton production, p. 69-90. In: V.S. Kennedy, [Ed.], Estuarine Comparisons, Academic Press, New York.
- Boynton, W.R., W.M. Kemp and C.G. Osborne. 1980. Nutrient fluxes across the sediment-water interface in the turbid zone of a coastal plain estuary, p. 93-109. In: V.S. Kennedy, [Ed.], Estuarine Perspectives, Academic Press, New York.
- Boynton, W.R., W.M. Kemp, C.G. Osborne, E. Spalding, C.W. Keefe and K.V. Wood. 1982b. Estuarine community dynamics in relation to power plant operations. [UMCEES] CBL Ref. No. 82-78. Solomons, MD
- Boynton, W.R. and F.M. Rohland. 1990. Ecosystem Processes Component (EPC) Data Dictionary. [UMCEES] CBL Ref. No. 90-029. Solomons, MD
- Boynton, W.R., *et al.* 1984. Ecosystems Processes Component Study Plan. [UMCEES] CBL Ref. No. 85-16. Solomons, MD
- Boynton, W.R., *et al.* 1989. Ecosystem Processes Component Level 1 Interpretive Report No. 6. [UMCEES] CBL Ref. No. 89-080. Solomons, MD
- Boynton, W.R., J.H. Garber, W.M. Kemp and R. Summers. 1991. Patterns of nitrogen and phosphorus input, storage, recycling and fate in selected portions of Chesapeake Bay and selected tributary rivers. Draft Manuscript. Chesapeake Biological Laboratory, Solomons, Md 20688
- Boynton, J. E. 1985. The influence of current velocity on nutrient and oxygen exchanges between estuarine sediments and the water column. Ph.D. Thesis. University of Maryland, Marine Estuarine Environmental Sciences.
- D'Elia, C.F., D.M. Nelson, and W.R. Boynton. 1983. Chesapeake Bay nutrient and plankton dynamics: III. The annual cycle of dissolved silicon. *Geochim. Cosmochim. Acta* 47:1945-1955.
- D'Elia, C. F., J. G. Sanders, and W. R. Boynton. 1986. Nutrient enrichment studies in a coastal plain estuary: phytoplankton growth in large-scale, continuous cultures. *Can. J. Fish. Aquat. Sci.* 43:397-406.
- Dugdale, R. C. and J. J. Goering. 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnol. Oceanogr.* 12:196-206.
- Garber, J.H. *et al.* 1989. Ecosystem Processes Component and Benthic Exchange and Sediment Transformations. Final Data Report. Maryland Department of the Environment. Maryland Chesapeake Bay Water Quality Monitoring Program. [UMCEES] CBL Ref. No. 89-075. Solomons, MD
- Hammond, D.E., *et al.* 1985. Benthic fluxes in San Francisco Bay. *Hydrobiologia* 129:69-90.
- Hargrave, B.T. 1969. Similarity of oxygen uptake by benthic communities. *Limnol. Oceanogr.* 14:801-805.
- Holland, A.F., A.T. Shaughnessy, L.C. Scott, B.A. Dickens, J. Gerritsen and J.A. Ranasinghe. 1989. Long term benthic monitoring and assessment program of the Maryland portion of Chesapeake Bay: Interpretive Report (Prepared for the Maryland Department of Natural Resources). VERSAR Inc., 1900 Rumsay Road, Columbia MD 21045. CBRM-LTB/EST 89-2.

- Jensen, M. H., E. Lomstein, and J. Sorensen. 1990. Benthic NH_4 and NO_3 flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. *Mar. Ecol. Prog. Ser.* 61:87-96.
- Kelly, J. R. and S. W. Nixon. 1984. Experimental studies on the effect of organic deposition on the metabolism of a coastal marine bottom community. *Marine Ecology Progress Series* 17:157-169.
- Kemp, W.M. and W.R. Boynton. 1980. Influence of biological and physical factors on dissolved oxygen dynamics in an estuarine system: implications for measurement of community metabolism. *Estuar. Coast. Mar. Sci.* 11:407-431.
- Kemp, W.M. and W.R. Boynton. 1981. External and internal factors regulating metabolic rates of an estuarine benthic community. *Oecologia* 51:19-27.
- Kemp, W.M. and W.R. Boynton. 1984. Spatial and temporal coupling of nutrient inputs to estuarine primary production: the role of particulate transport and decomposition. *Bull. Mar. Sci.* 35:522-535.
- Klump, J.R. and C.S. Martens. 1981. Biogeochemical cycling in an organic rich coastal marine basin. II. Nutrient sediment-water exchange process. *Geochim. Cosmochim. Acta.* 45:101-121.
- Krom, M.D. and R.A. Berner. 1980. The diffusion coefficients of sulfate, ammonium and phosphate ions in anoxic marine sediments. *Limnol. Oceanogr.* 25:327-337.
- Malone, T.C., L.H. Crocker, S.E. Pike, and B.W. Wendler. 1987. Influences of river flow on the dynamics of phytoplankton production in a partially stratified estuary. *EOS* 68:1688.
- Nixon, S.W. 1981. Remineralization and nutrient cycling in coastal marine ecosystems, p. 111-138. In: B.J. Neilson and L.E. Cronin [Eds.], *Estuaries and Nutrients*, Humana Press, Clifton, New Jersey.
- Nixon, S.W., J.R. Kelly, C.A. Oviatt, and S.S. Hale. 1976. Nitrogen regeneration and the metabolism of coastal marine bottom communities. In: Anderson, J.M. and A. MacFadden, (Eds.), *The role of terrestrial and aquatic organisms in decomposition processes. The 17th Symposium of the British Ecological Society.* Blackwell, Oxford, p. 269-283.
- Roden, E.E. 1990. Sediment sulfur cycling and its relationship with carbon cycling and oxygen balance in the Chesapeake Bay. PhD Dissertation. MEES Program, University of Maryland.
- Sellner, K. et. al. 1989. Long term phytoplankton monitoring and assessment program. Maryland Chesapeake Bay Water Quality Monitoring Program. Benedict Estuarine Research Laboratory, Benedict, MD.
- Summers, R.M. 1989. Point and Non-point Source Nitrogen and Phosphorus loading to the Northern Chesapeake Bay. Maryland Department of the Environment, Water Management Administration, Chesapeake Bay and Special Projects Program. Technical Report, Baltimore MD
- Twilley, R. R. and W. M. Kemp. 1987. Estimates of sediment denitrification and its influence on the fate of nitrogen in Chesapeake Bay. Technical Series No. TS-51-86, Center for Environmental and Estuarine Studies, University of Maryland, Cambridge, MD 21613.
- Yamada, S.S. and C.F. D'Elia. 1984. Silicic acid regeneration from estuarine sediment cores. *Mar. Ecol. Prog. Ser.* 18:113-118.
- Zeitzschel, B. 1980. Sediment water interactions in nutrient dynamics. In: Tenore, K.R., and B.C. Coull (Eds.), *Marine benthic dynamics.* University of South Carolina Press, Columbia, SC, p. 219-242.