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UNIVERSITY OF MARYLAND CENTER for ENVIRONMENTAL SCIENCE
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Sediment Oxygen and Nutrient Exchange Measurements from Chesapeake Bay, Tributary Rivers and Maryland Coastal Bays:

Development of a Comprehensive Database

&

Analysis of Factors Controlling Patterns and Magnitude of Sediment-Water Exchanges

June 2008

A Program Supported by:

Maryland Department of the Environment
Science Services Administration
TMDL Technical Development Program
1800 Washington Blvd. Suite 540
Baltimore, MD 21203

Technical Report Series No. TS-542-08 Ref. No. [UMCES]CBL 08-019
University of Maryland
Center for Environmental Science

Sediment Oxygen and Nutrient Exchange Measurements from Chesapeake Bay, Tributary Rivers and Maryland Coastal Bays:

Development of a Comprehensive Database & Analysis of Factors Controlling Patterns and Magnitude of Sediment-Water Exchanges

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June, 2008

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Executive Summary

During the past several decades much has been learned about the effects of nutrient inputs (e.g., nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance, sediment nutrient and oxygen dynamics and oxygen conditions in deep waters. While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues.

Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production and algal blooms are partially sustained through summer and fall periods by benthic recycling of essential nutrients, (3) deposition of organic matter from surface waters to estuarine sediments links these processes of production and consumption, (4) the relative importance of sediment processes of oxygen consumption and nutrient release on full water column plus sediment metabolism is inversely proportional to water depth, and (5) primary environmental factors regulating the seasonal pattern and magnitude of sediment processes include temperature, sediment redox conditions, benthic community composition and labile organic matter supply rates. Many of the results contained in this report use these findings as points of departure for analysis of Chesapeake Bay sediment oxygen and nutrient dynamics.

There are a number of goals we wished to achieve in preparing this document. First, we and others have been making measurements of sediment processes in Chesapeake Bay and tributary rivers since 1978 and measurements continue through the present time. During this time about 300 different sites were occupied for sediment flux measurements and these sites were located in about 27 tributary rivers and the mainstem Bay. A total of over 6000 individual analyte fluxes were generated during these years. Thus, we had an opportunity to produce a comprehensive summary of Chesapeake Bay benthic flux work. Second, given the size of this data set, we had the opportunity to examine the data for general characteristics of Chesapeake sediment fluxes, region-specific flux characteristics (e.g., tidal fresh versus mesohaline), and factors influencing the magnitude and seasonal patterns of these processes. Third, we assembled sediment fluxes from 48 other estuarine locations around the world (Bailey 2005) and had the opportunity to compare and contrast these with those from the Chesapeake Bay. Finally, we packaged the Chesapeake Bay sediment flux data in a database software program (Microsoft Access) so that these data can be used as needed by the larger community of estuarine ecologists, sediment biogeochemists, and water quality modelers.

This Executive Summary lists important results generated from this analysis and these are provided below, arranged by Report Chapters 2 through 12.

Chapter 2

- There has been a multi-decade evolution in scientific thinking concerning nutrient cycling in estuarine environments in which the importance of sediments has now been fully recognized. Water quality models have incorporated more or less sophisticated components to account for sediment processes.
- The number of analytes measured in estuarine sediment flux studies has expanded beginning with just SOC (sediment oxygen consumption) measurements in the early years and then coming to include dissolved N, P and Si compounds. Even more recently (but not in this data set) CO_2, CH_4, N_2 and N_2O flux measurements have become more common but are still not a routine part of most sediment flux monitoring programs. They should be included both for reasons of increasing our understanding of these processes and for use as very strong indicators of response to restoration efforts.
- While there were some sediment flux measurements made in Chesapeake Bay during the 1970's, routine measurements did not begin until the mid-1980's and continued through 2005. There are no sediment flux measurements available for the Maryland portion of Chesapeake Bay or Maryland tributary rivers before the Bay and tributary rivers were exhibiting strong signs of anthropogenic eutrophication.
- The data set contains primarily measurements made during a single year with sampling focused on summer periods. However, there were three sediment flux programs where time-series flux data were developed and these include work in the upper Bay, the Maryland Biomonitoring Program work at 8-10 sites in the Bay and tributary rivers and the NSF-LMER work in the mainstem Bay.

Chapter 3

- The majority of the data used in this analysis came from Dr. W. R. Boynton research group studies funded by Maryland Department of the Environment, Maryland Department of Natural Resources, National Science Foundation and Maryland Environmental Services. Data was obtained from electronic storage where available and directly from raw datasheets and reports when not.
- Peer reviewed literature was searched using the *Aquatic Sciences and Fisheries Abstracts* (ASFA) database covering articles published in 1978 to 2006.
- Non-peer reviewed sources were also searched including the Virginia Institute of Marine Science's *Bibliography of Chesapeake Bay Grey Literature/ Chesapeake Bay Reports* which includes more than 70,000 pages of scientific papers, reports, technical notes or other documents produced and published by governmental agencies, academic institutions and other groups that are not distributed or indexed by commercial publishers (VIMS Libraries: http://www.vims.edu/GreyLit).
- Data were also obtained and verified through personal communication with researchers known to have made sediment oxygen and nutrient exchange measurements in the Chesapeake Bay region.

- Data were gathered for sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite + nitrate (NO_2^- + NO_3^-) and dissolved inorganic phosphorus (PO_4^-) flux between sediments and overlying waters. Associated site data was also collected (if available) and all data were converted to standard units.
- Only flux data generated using direct constituent measurement (rather than estimates from pore water profiles or modeling) were used for this review. Sediment exchange data were included from measurements made using either shipboard or laboratory mesocosm experiments (intact sediment cores incubated in a laboratory setting) or benthic chambers (domes or boxes placed on top of areas of sediment *in situ*). Only measurements made in the dark and under ambient conditions (e.g., water temperature, salinity) were used. Data were arranged according to individual reference and assigned an estuary name and corresponding source code.
- Locations included 290 individual stations throughout the Chesapeake Bay, its tributaries and Maryland's Coastal Bays. TMDL sampling (June, July and August of one year) includes 138 of the stations.

Chapter 4

- The flux data set for Chesapeake Bay, tributary rivers and the Maryland Coastal Bays contains measurements from a high diversity of environments. Included are high, moderate and low salinity areas, normoxic, hypoxic and near-anoxic sites and shallow, moderate and deep water sites.
- Sediment flux measurements were made in all months of the year but the majority of measurements (72%) were made during the June - August period. Thus, the data set focuses on summer fluxes. However, measurements made during cool and cold periods of the year clearly indicated that sediment fluxes of DO, N and P compounds were much smaller during those periods.
- Descriptive statistics and frequency histograms have been developed using the entire flux data set for each flux and each environmental variable. Most exhibited substantial ranges of values, as expected, given widely differing sediment and water column conditions.
- Compared to "new inputs" of N and P compounds, sediment nutrient releases in Chesapeake Bay are large, comparable to external nutrient loading rates to moderately to very nutrient enriched ecosystems.

Chapter 5

- Among 13 different Bay tributary and mainstem locations there was considerable diversity in spatial patterns and magnitude of sediment fluxes. Such a result was expected given the diversity of tributaries sampled and the water and sediment quality of these systems. However, in most cases, the patterns of flux along salinity, depth, DO and sediment redox gradients conformed to our conceptual model of factors regulating sediment flux patterns and magnitude. In most tributary and mainstem Bay sites, sediment fluxes of oxygen, N and P exerted a considerable influence on water quality conditions. It is expected that these fluxes will decrease if nutrient loading to these systems decrease.

- We constructed an index for sediment fluxes. We ranked fluxes from each system from one to 12 with the highest flux values ranked as one and the lowest flux values ranked 12. The rankings for the four fluxes (SOC + NH_4 + NO_2 and NO_3 + PO_4) were added together to obtain the summer sediment flux index. This index could range from 4 to 48. The results of this exercise suggest that sediment conditions largely predict the magnitude of sediment fluxes for this group of Chesapeake Bay tributaries and mainstem. For example, the Coastal Bays, Elk, Sassafras and Pocomoke Rivers rank high in terms of sediment conditions. Conversely, the Severn, mainstem Bay, Patapsco, Potomac, Corsica and Patuxent Rivers rank low in terms of sediment conditions. Other sites are intermediate. The sediment flux index closely corresponded with the sediment condition index. This result suggests that many of the important features of sediment condition and flux have been captured in these monitoring efforts. It is useful to have a simple index that provides first-order indications of sediment conditions and the likely nature and magnitude of sediment fluxes.

Chapter 6

- The majority of sediment flux measurements (72%) were collected during the summer months (June - August) when sediment processes are most active; about 12% of measurements were made during spring and the same percentage during fall. Only 5% of all measurements were made during winter.
- There were very strong seasonal patterns of flux for SOC, NH_4, PO_4 and NO_2 + NO_3. SOC and NO_2 + NO_3 fluxes peaked during late spring - early summer and NH_4 and PO_4 fluxes peaked during summer. Winter rates were always low for all sediment fluxes and low enough to have little influence on water quality conditions.
- There is clear evidence of strong temperature effects on sediment fluxes. Calculated Q_{10} values were generally in the range of 1.5 to 3.5 with a few higher values. These values compared well with Q_{10s} computed for other estuarine and coastal marine environments.
- However, it also appears that in some portions of the Bay and tributary rivers the temperature - flux relationship fails later in summer and fall. Late summer and fall sediment fluxes are often lower than those observed in late spring and early summer at similar temperatures.
- Analyses of sediment flux time-series data in several areas of the Bay indicate that the supply rate of labile organic matter to sediments is a master variable constraining the magnitude of summer and early fall fluxes. Other environmental conditions (e.g., temperature, sediment redox conditions) modify the timing and other characteristic of sediment flux but labile organic matter supply rate ultimately constrains these processes.
- The last two conclusions suggest that there is little nutrient memory in the Bay. Water quality modelers should not take the liberty of using nutrients stored in sediments to influence water quality conditions much beyond a single year. Our analyses suggest that the "sediment flux clock" is set each year with the deposition to the sediment surface of spring bloom organic matter (and

supplemented to a lesser degree by summer bloom deposition) with little influence from deposition events in previous years.

Chapter 7

- Despite a relatively small range in depths (1-42 m) strong relationships between depth and SOC were evident in the full data set and in selected areas of the Bay. This finding is consistent with several earlier examinations of this issue where far greater depth ranges were considered. The SOC-depth relationship appears quite robust
- The general explanation for this relationship is that the amount of euphotic zone organic matter which sinks to the sediment surface to support SOC decreases as longer water columns increase the transit time (and attendant opportunity for consumption by heterotrophic plankton) for sinking substrates. In short, in deeper water columns animals eat most of the sinking material before it gets to the bottom
- Water column respiration rates have been grossly under-measured in the Bay and tributary rivers. With available data it is clear, however, that water column respiration is a major term in oxygen budgets and deserves much more attention.
- As previously reported for other coastal and estuarine systems the relative importance of SOC compared to water column respiration is also a function of depth in Chesapeake Bay and tributary rivers. At depths < 4 m SOC dominated community respiration and the importance of SOC decreased with additional depth.
- Water quality models should be able to reproduce the empirical relationships between SOC, water column respiration and depth developed in this synthesis

Chapter 8

- During summer periods sediment P releases can have a large impact on water quality conditions. It appears that in areas of the Bay and tributary rivers with some salt content in overlying waters, sediment P fluxes can supply enough P to support modestly high rates of plankton production. These rates are as large (or larger in some cases) than input rates of P from terrestrial sources and sediment P releases are in a chemical form (DIP) ready for immediate utilization by biota.
- It appears that sediment P flux is greatly enhanced under poor water quality conditions of low DO in bottom waters and low sediment redox conditions.
- In a few localized areas of the Bay (e.g., upper Potomac River estuary) elevated water column pH can lead to elevated sediment P releases. We do not think this is an important mechanism in most areas of the Bay because waters are well buffered against large pH changes.
- Limited experimental work indicates that sediments are responsive, on short time scales (hours to a few days) to changes in both pH and sediment DO and redox conditions. Sediments responded to sharply increased pH in a matter of hours and to very depressed DO conditions in 2-3 days.
- While there appears to be a large stock of P in sediments, experimental studies indicated that sediments from the mesohaline mainstem Bay could be depleted in available P in a matter of a month or two when exposed to very low DO

conditions and no new organic matter or sediments was reaching the sediment surface. This suggests that the sediment P memory is not long as is the case in many eutrophic lakes.

Chapter 9

- A conceptual model was developed indicating likely linkages between nutrient loading rates and sediment biogeochemical responses. This is an essential step for management since one of the primary goals of the Chesapeake Bay Program is to reduce nutrient loading rates to the Bay system. This model and subsequent analyses indicate that sediment fluxes should track nutrient loading rates.
- Multiple analyses indicate links to sediment processes from distal (inputs) and more proximal (plankton production, organic matter deposition rates) causative factors, again as suggested by the conceptual model.
- There are strong indications that the magnitude and pattern of sediment processes respond to causative factors on annual rather than longer time scales. This suggests responsive sediment process rather than processes that have longer time constants.
- Comparisons of nutrient loads from external sources (e.g., diffuse and point sources) to sediment nutrient releases indicate they are about equal in magnitude. Thus, if just these two processes are considered, the load from the land is doubled because sediments recycle an amount of N about equal to the annual load from external sources.

Chapter 10

- Examination of estuarine nutrient storages indicate that most of the N and P in these systems are contained in bottom sediments. If there is a reactive nutrient storage (nutrient memory) then it is clearly located in the bottom sediments.
- It is often assumed that there is a long nutrient memory in these shallow estuarine systems because nutrients loads have been elevated for 4-5 decades and longer in some cases. The management implication of this is that these systems will not rapidly respond to nutrient load reductions.
- Examination of both water column and sediment flux time series data and laboratory experimental data suggest that sediment fluxes are maintained by very recent delivery of labile organic matter. Sediment fluxes appear to respond to changes in organic matter supply rates on time scale of weeks to months rather than years to decades. If large changes in nutrient loads occur we would predict rapid changes in sediment oxygen and nutrient fluxes and rapid improvement in water quality
- Water quality models need to have sediment flux components that are responsive to changes in labile organic delivery rates to sediments. Models that have non-responsive sediment components are probably not accurate and should be replaced.

Chapter 11

- Bottom water DO conditions have a clear impact on sediment N biogeochemistry.
- Indirect methods of analysis indicate that when sediments are exposed to normoxic conditions nitrogen is lost from the system, presumably via coupled nitrification-denitrification.
- Very limited but direct measurements of both routine sediment N fluxes and denitrification support this concept wherein N is lost in normoxic sediments.
- If bottom water DO conditions improve we would expect a significant decrease in sediment N recycling efficiency.

Chapter 12

- Several statistical analyses suggest a few important water quality variables have strong influence of sediment flux. These variables include bottom water DO, temperature, sediment Eh, and water column nitrite plus nitrate concentrations and these variables appear to be important in all salinity zones of the Bay and tributary rivers
- It is very likely that organic matter deposition rates, particularly during spring, set the upper limit on sediment flux and further modify the nature of sediment flux. We do not have estimates of spring deposition at most sites so this important process is not directly included in these analyses. However, results of other analyses indicated the importance of organic matter deposition rates to the sediment surface.
- The conceptual model of sediment flux is consistent with results of these statistical analyses. It also appears that modest improvement in deep water DO conditions (to > 3-4 mg L^{-1} during summer) would strongly modify sediment flux such that nutrient recycling rates would decrease and thus contribute to improved water quality conditions.

Chapter 1

Introduction

1-0. Overview

During the past several decades much has been learned about the effects of both natural and anthropogenic nutrient inputs (e.g., nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance, sediment nutrient and oxygen dynamics and oxygen conditions in deep waters (Nixon 1981; Boynton et al 1982; Kemp et al 1983; D'Elia et al 1986; Nixon 1988; Kemp and Boynton 1992; Malone 1993; Cloern 2001; Kemp et al 2005). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues.

Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production and algal blooms are partially sustained through summer and fall periods by benthic recycling of essential nutrients, (3) deposition of organic matter from surface waters to estuarine sediments links these processes of production and consumption, (4) the relative importance of sediment processes of oxygen consumption and nutrient release on full water column plus sediment metabolism is inversely proportional to water depth, and (5) primary environmental factors regulating the seasonal pattern and magnitude of sediment processes include temperature, sediment redox conditions, benthic community composition and labile organic matter supply rates.

Many of the results contained in this report use these findings as points of departure for analysis of Chesapeake Bay sediment oxygen and nutrient dynamics.

1-1. Conceptual Model of Estuarine Nutrient and Water Quality Processes

To place the sediment flux analyses presented here in a larger context we use a conceptual model of estuarine and water quality processes. In this conceptual model (Fig. 1-1; adapted from Kemp et al 2004) nutrients and organic matter enter the Bay from a variety of sources, including wastewater treatment plant effluents, fluvial inputs, non-point drainage and direct rainfall on Bay waters. Dissolved nutrients are rapidly incorporated into particulate matter mainly via biological processes but chemical and physical mechanisms are also involved (e.g., P adsorption to sediment particles). A portion of this newly produced organic matter eventually sinks to the bottom, decomposes and, if of sufficient magnitude, contributes to the development of hypoxic or anoxic conditions in deep waters and at the sediment-water interface. This results in a loss of benthic habitat for important infaunal, shellfish and demersal fish communities. The regenerative and large nutrient storage capacities of estuarine sediments ensure a large return flux of nutrients from sediments to the water column that can sustain continued high rates of phytoplanktonic growth and biomass accumulation. Continued phytoplanktonic growth and accumulation supports high rates of organic matter deposition to deep waters and estuarine sediments, creating and sustaining hypoxic and anoxic conditions typically associated with eutrophication of estuarine systems. It further

appears that when severe hypoxic or anoxic conditions are established at the sediment-water interface there are changes in the biogeochemistry of both N and P which act to further promote eutrophication tendencies.

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

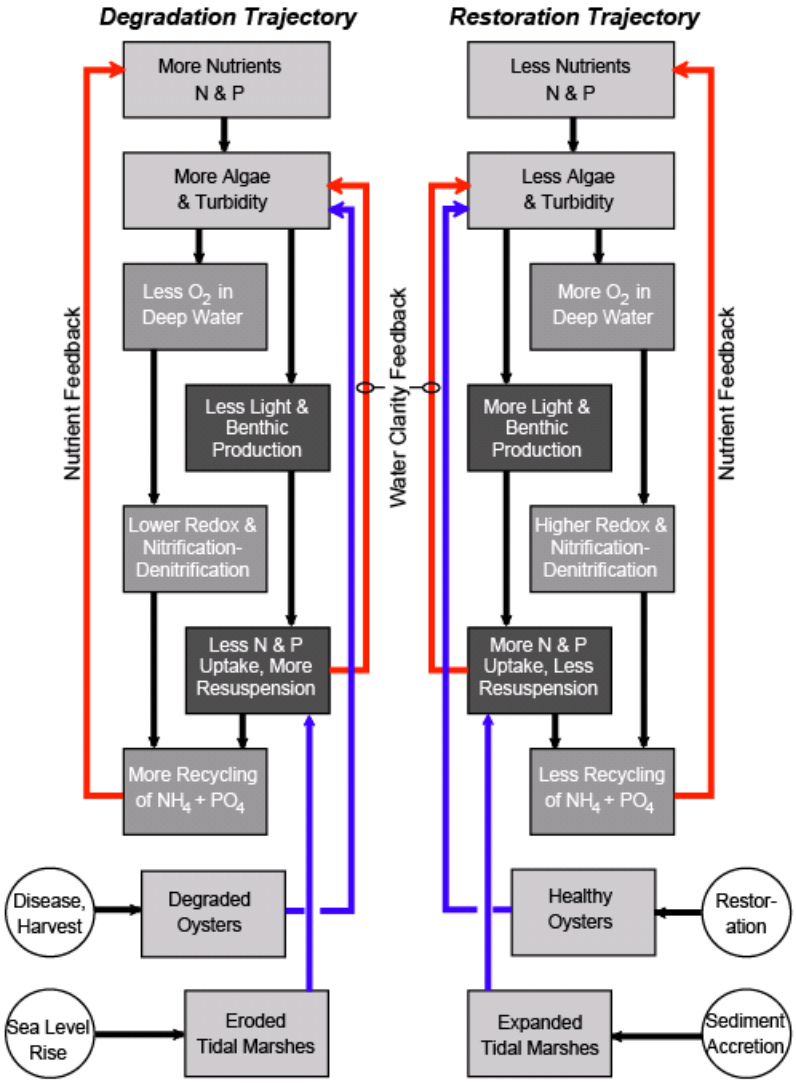

Figure 1-1. *A conceptual model of nutrient induced eutrophication for estuaries such as Chesapeake Bay. Note that there are both degradation and restoration trajectories. Of particular importance here are the positive feedbacks induced by low oxygen conditions on sediment-water nutrient processes. This diagram was developed by Kemp et al (2005).*

quality and habitat conditions. The schematic model summarizes this conceptualization of estuarine eutrophication where increased nitrogen (N) and phosphorus (P) loads result in a water quality degradation trajectory and reduced nitrogen and phosphorous loads lead to a restoration trajectory.

1-2. Magnitude of Nutrient Loading to Estuarine Systems

Since nutrient loading to estuarine systems is a focus of restoration efforts and because the conceptual model of eutrophication of Chesapeake Bay suggests an important role of sediment oxygen and nutrient processes we have included here a general description of nutrient loading rates for many estuarine systems, including multiple areas of the Bay system. Later in this report we present an analysis relating external nutrient loading rates to sediment processes. Thus, this section provides an overview of one of the main processes, external nutrient inputs, influencing sediment oxygen and nutrient dynamics.

Both the scope and detail of information currently available concerning nutrient inputs to coastal and estuarine waters has changed dramatically since the early work of Meybeck (1982) who reported strong correlations between N concentrations and features of drainage basins (e.g., population density) for 30 rivers. During the late 1980s NOAA organized nutrient load estimates for many estuaries in the USA (e.g., Bricker et al 1999). More recently, Smith et al (2003) updated the global-scale analysis of Meybeck (1982) using data from 165 rivers to demonstrate that: (1) N and P loads were statistically related to population density and runoff per unit land area, (2) N and P loads were closely correlated to each other despite different biogeochemistries, (3) loads to coastal waters had increased by a factor of about three since the 1970s. Estimates of future loads to estuaries and the coastal ocean suggest another doubling by 2050 (e.g., Kroeze and Seitzinger 1998).

Several recent analyses of nitrogen loads to estuarine systems have been based on direct measurements of loads from riverine and point sources. For example, Conley et al (2000) reported N loading rates to 81 Danish estuaries for a 7 year period, Nedwell et al (2002) reported DIN loads to 93 mainland United Kingdom estuaries and Carmichael et al (2004) estimated N loads to 15 small Cape Cod estuaries. In addition, estimates of historical N loads suggest 5-fold or larger increases during the last three centuries for both Narragansett Bay (Nixon 1997) and Chesapeake Bay (Boynton et al 1995). Recent estimates for Chesapeake (Hagy et al 2004) and Waquoit Bay (Bowen and Valiela 2001) suggest more than a doubling of N loads during the previous half-century. Nixon (2003) estimated Nile River nutrient loads to the adjacent Mediterranean sea coast before and after construction of the Aswan High Dam and argued that the loss of nutrients inputs due to damming of the Nile in the 1960s has largely been replaced by anthropogenic inputs associated with run-off of agricultural fertilizers and sewage discharges.

To examine the distribution of N-loading rates among well-studied estuaries, Boynton and Kemp (2008) organized a frequency histogram of N loads for 218 estuarine systems. The distribution that emerged indicated that most N-loading rates fell within the range of 6-50 g N m^{-2} yr^{-1}, and only about 15% of the systems had loading rates below 5 g N m^{-2} yr^{-1}. It is interesting to note that anthropogenic N dosing to major watersheds of the USA ranged from 0.5 to 3.5 g N m^{-2} yr^{-1} (Jordan and Weller 1996) and from 0.9 to about 6 g N m^{-2} yr^{-1} for smaller watersheds of USA coastal areas (Van Breemen et al

2002; Castro et al 2003). The anthropogenic rates of N-loading to adjacent estuarine systems are clearly much higher; 37% of the sample organized by Boynton and Kemp (2008) exceeded 50 g N m^{-2} yr^{-1}, almost an order of magnitude greater than most adjacent land areas. Thus, it appears that estuaries, including many portions of the Bay, are among the most heavily fertilized systems on the planet.

Boynton et al (2008) also assembled data for 34 estuaries where inputs of both TN and TP (g N or P m^{-2} yr^{-1}) were available (Fig. 1-2). There is a very large range in N and P inputs among these estuaries. N loads varied by a factor of almost 200 and P by just over 300; the majority of systems in this sample had N and P loading rates ranging from 5 to 50 and 1 to 10, respectively. Despite the different biogeochemistry of N and P, there was an obvious correlation between loading rates of these elements as reported by Smith et al (2003). Loading rates for a few systems (e.g., Himmerfjarden, Sweden; Back River, MD) had especially high N: P ratios because sewage was a major nutrient source and P, but not N, was removed at treatment facilities. In others, elevated N: P ratios were the result of diffuse source inputs that were naturally more enriched in N (mainly NO_3) than P. Finally, it is important to note that loading rates alone are not generally sufficient to predict the trophic status (*sensu* Nixon 1995) of an estuary. For example, both the

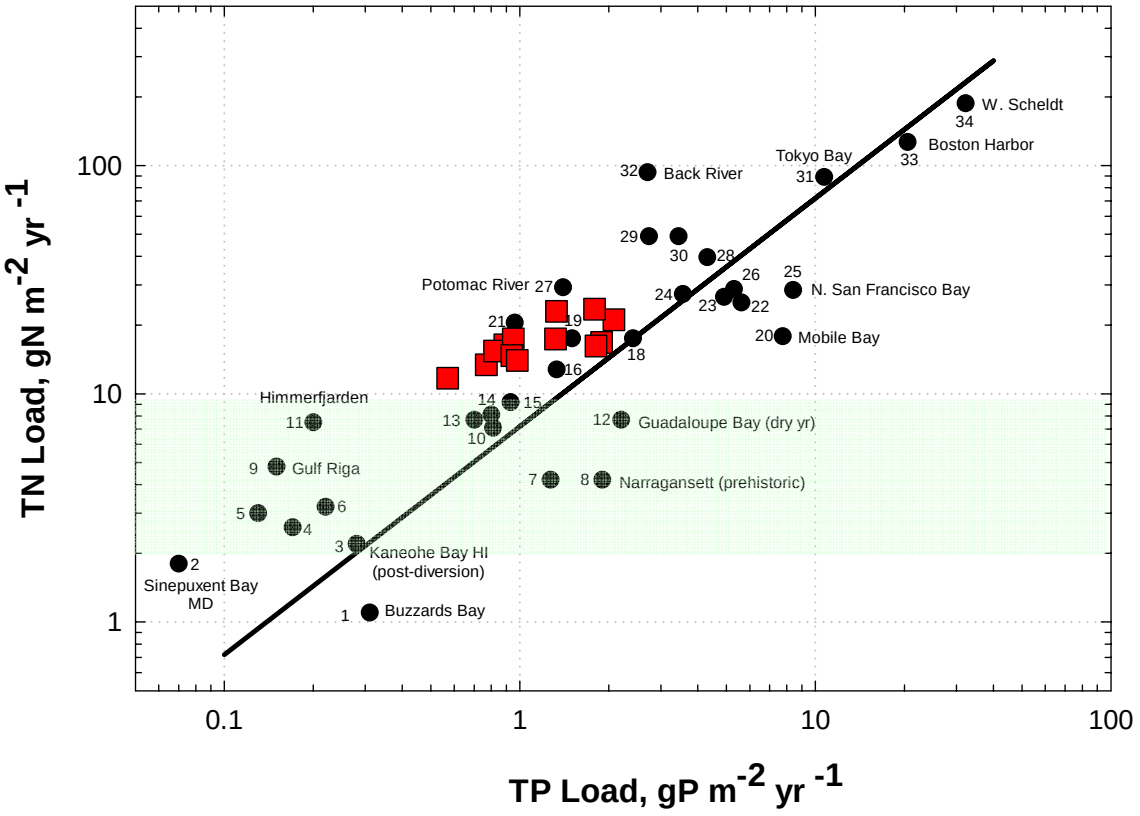

Figure 1-2. *A scatter plot of annual TN and TP loading rates for a variety of estuarine ecosystems including several from the Chesapeake Bay and Maryland Coastal Bays. The red squares indicate TN and TP loading rates for a 13 year period in the Patuxent River estuary. The pale green band indicates the range in N loading rates to a variety of Mid-Atlantic watersheds and suggests that loading rates to adjacent estuarine systems are indeed high. Figure was adapted from Boynton et al (2008).*

Potomac River estuary and Narragansett Bay had similar annual N loading rates but the Potomac exhibited severe eutrophication characteristics while these were far less severe in Narragansett Bay. Several authors have noted that estuarine morphology, water residence times, water column mixing rates, light conditions and biological communities all have potentially strong influences on the impact of loading rates (e.g., Wulff et al 1990; Boynton et al 1996; Valiela et al 2000**).** A 13 year record of annual TN and TP loads to the Patuxent River estuary was added to Figure 1-2 to serve as a reminder that inputs for many estuaries exhibit considerable inter-annual variability. In this example, TN and TP loads varied by factors of about 2.5 and 3.5, respectively. There was an indication that the TN:TP load ratio decreased during high load years, probably because more sediment, and sediment-bound P, were eroded and transported during wetter than average conditions. Thus, both the quantity and composition of nutrient inputs can vary due to climate variability.

1-3. Purpose of this Document

There are a number of goals we wish to achieve with the work contained in this document. First, we and others have been making measurements of sediment processes in Chesapeake Bay and tributary rivers since 1978 and measurements continue through the present time, although at a much reduced pace. During these years about 300 different sites were occupied for sediment flux measurements and these sites were located in about 27 tributary rivers and the mainstem Bay. A total of about 6000 individual analyte fluxes were generated during these years. Thus, we have an opportunity to produce a comprehensive summary of Chesapeake Bay benthic flux work. Second, given the size of this data set, possibly the most comprehensive of any in the world, and the generally consistent fashion in which data were collected, we have the opportunity to examine the data in a search of general characteristics of Chesapeake sediment fluxes, region-specific flux characteristics (e.g., tidal fresh versus mesohaline), and factors influencing the magnitude and seasonal patterns of these processes. Third, we have also assembled sediment fluxes from 48 other estuarine locations around the world (Bailey 2005) and we now have the opportunity to compare and contrast these with those from the Chesapeake Bay. Finally, we have packaged the Chesapeake Bay sediment flux data in a database software program (Microsoft Access) so that these data can be used as needed by the larger community of estuarine ecologists, sediment biogeochemists, and water quality modelers.

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Chapter 2

History of Sediment-Water Flux Measurements

2-1. Global View

Our understanding of nutrient processes in estuaries and the role sediments play in these processes has witnessed several periods of rapid expansion and elaboration. Over a quarter century ago Nixon (1981) reviewed available literature and concluded that our perspective on the importance of various components and mechanisms in the nutrient cycling scheme had changed remarkably. Earlier conceptual models emphasized the water column as the sole site of organic matter consumption and nutrient remineralization (Fig. 2-1a). One of the major changes during the next few decades was the widespread documentation of the importance of shallow sediments as an important source of recycled nutrients and oxygen consumption and as a likely site controlling the relative availability of N and P for photosynthesis. Boynton et al (1980) documented various aquatic environments where this appeared to be the case (Fig. 2-1b). Since the 1980s estimates have come available concerning rates of N and P burial in accreting sediments and the magnitude and factors controlling estuarine sediment denitrification and nitrous oxide production. There has also been a large expansion in the number of sediment-water exchange measurements made of the type reported here (Bailey 2005).

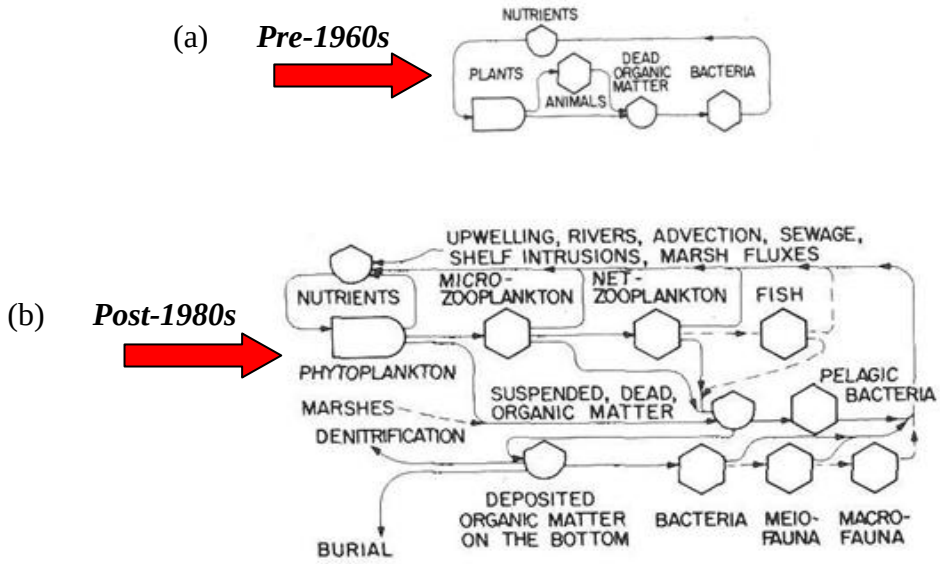

Figure 2-1. *Conceptual diagrams of remineralization and nutrient cycling in coastal and estuarine systems during the pre-1960s and post-1980s periods where the former emphasized water column processes and the latter was elaborated to include benthic storages and processes. These diagrams were developed by Nixon (1981).*

More recently, Bailey (2005) compiled sediment-water flux information from the published literature from about 50 different estuarine and coastal marine systems, again indicating the increased appreciation of sediment processes in the general functioning of these systems. In this effort Bailey (2005) reported a total of about 700 sets of fluxes (some authors reporting just SOC while others reported fluxes of SOC and N and P). As we shall see, there are many more flux measurements available for Chesapeake Bay and tributaries rivers than all other sites combined. During the past decade or so there has been an elaboration in the number of analytes measured (now often including N_2 and N_2O and CO_2 in addition to the commonly measured fluxes of O_2, N and P compounds), a strong shift away from in-situ chamber measurements to shipboard incubated sediment cores and more experimental manipulations of cores.

2-2. Chesapeake Bay Sediment Fluxes

The exact early history of sediment flux work in Chesapeake Bay is as cloudy as the water where many of these measurements were made. The reason for this is that some early measurements were largely exploratory or measured only SOC. Others may be buried in technical reports that have not seen the light of day for decades and we have not yet found them. It remains possible that a few have simply faded from memory although this seems unlikely at this point. However, it is clear that sediment flux work in Chesapeake Bay began in the late 1970s and the first published works were done in the Potomac (Callender 1982), Patuxent (Boynton et al 1980) and York River (Pheol 1981; Rizzo 1990). Boynton and Kemp (1985) reported sediment fluxes from the mainstem Bay and several tributaries based on measurements made in 1980 and 1981. However, routine measurements of sediment oxygen and nutrient fluxes did not begin until 1984 (trial measurements) - 1985 (reported measurements) when the Maryland portion of the Chesapeake Bay Biomonitoring Program began operations with 10 sites distributed between the mainstem Bay and tributary rivers and visited 4-6 times a year (encompassing the months of April-November). This measurement program continued through 1996 and is the longest time-series data set available. In 1988-89 the Chesapeake Bay Program also supported scattered sediment flux measurements throughout the mainstem Bay for purposes of calibrating the sediment component of the Bay water quality model. Also beginning in 1989 the NSF Land Margins Ecosystem Research (LMER) program supported seasonal measurements at three primary sites along the mainstem Bay for a five-year period. The Maryland Environmental Services supported sediment flux measurements in the upper Bay and Baltimore Harbor throughout the 1990s in support of proposed and on-going channel dredging operations. Finally, Maryland Department of Environment, beginning in 1999, began supporting sediment flux studies in all of the major tributaries of Maryland with three measurements made during the summer period and with 20-25 sites being visited in major tributaries and 2-6 stations in small tributaries. In all, sites in 22 different Maryland tributary rivers and the Maryland Coastal Bays were sampled before the program concluded in 2005. The vast majority of sediment flux measurements were supported by the Maryland Biomonitoring Program and the Maryland Department of Environment. About 93% of all flux measurements in the data set were collected by scientists of the University of Maryland's Center for Environmental Science.

2-3. "Take-Home" Summary

- There has been a multi-decade evolution in thinking concerning remineralization and nutrient cycling in estuarine environments in which the importance of sediments has now been fully recognized. Water quality models have incorporated more or less sophisticated components to account for sediment processes.
- There has also been a shift from in-situ to shipboard measurement techniques with the latter being far more efficient in terms of sampling and more amenable to experimental manipulation.
- The number of analytes measured in estuarine sediment flux studies has expanded beginning with just SOD measurements in the early years and then coming to include dissolved N, P and Si compounds. Even more recently (but not in this data set) CO_2, CH_4, N_2 and N_2O flux measurements have become more common but are still not a routine part of most sediment flux monitoring programs. They should be included both for reasons of increasing our understanding of these processes and for use as very strong indicators of response to restoration efforts.
- While there were some sediment flux measurements made in Chesapeake Bay during the 1970s, routine measurements did not begin until the mid-1980s and continued through 2005. There are no sediment flux measurements available for the Maryland portion of Chesapeake Bay or Maryland tributary rivers before the Bay and tributary rivers were exhibiting strong signs of anthropogenic eutrophication. In short, there are no non-eutrophic baseline measurements of sediment flux available.
- The data set contains primarily measurements made during a single year with sampling focused on summer periods. These measurements, largely supported by MDE, MD-DNR and the NSF have greatly expanded the spatial coverage of sediment fluxes. However, there are also three sediment flux programs where time-series flux data were developed and these include the MES-supported work in the upper Bay, the Maryland Biomonitoring Program work at 8-10 sites in the Bay and tributary rivers and the NSF-LMER work in the mainstem Bay.

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Chapter 3

Data Sources, Management and Quality Assurance / Control Procedures

3-1. Data Sources

The majority of the data used in this analysis came from Boynton group studies funded by Maryland Department of the Environment, Maryland Department of Natural Resources, National Science Foundation and Maryland Environmental Services. Data was obtained from electronic storage where available and directly from raw datasheets and reports when not. A list of the companion reports for these data sources is included in section 3.-8 of this chapter.

Peer reviewed literature was searched using the *Aquatic Sciences and Fisheries Abstracts* (ASFA) database covering articles published in 1978 to 2006. This database is the primary indexing and abstracting service for marine science literature. The database includes ASFA Biological Sciences and Living Resources, ASFA Ocean Technology, Policy and Non-living Resources, ASFA Aquatic Pollution and Environmental Quality, ASFA Aquaculture and ASFA Marine Biotechnology (UMCES Libraries: http://www.cbl.umces.edu/Library/umcesdbs.php3). The database also includes graduate theses and dissertations and these were included for this review. Non-peer reviewed sources were also searched including the Virginia Institute of Marine Science's Bibliography of Chesapeake Bay Grey Literature/ Chesapeake Bay Reports which includes more than 70,000 pages of scientific papers, reports, technical notes or other documents produced and published by governmental agencies, academic institutions and other groups that are not distributed or indexed by commercial publishers (VIMS Libraries: http://www.vims.edu/GreyLit). Data were also obtained and verified through personal communication with researchers known to have made sediment oxygen and nutrient exchange measurements in the Chesapeake Bay region. Data source citations are found in section 3-8 of this chapter.

3-2. Inclusion Criteria

Data were gathered for sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite + nitrate (NO_2^- + NO_3^-) and dissolved inorganic phosphorus (PO_4^-) flux between sediments and overlying waters. Associated site data was also collected (if available) and all data were converted to standard units (Table 3-1).

Table 3-1. *Data parameters, standard units and database field names.*

Parameter	**Units**	**Database Field Name**
Station Name	Text	Station
Station Location Coordinates	DD.dddd (decimal degrees)	Latitude/Longitude
Time	hh:mm	Time
Date	m/dd/yyyy	Date
Station Total Depth	meters	Station Depth
Secchi Depth	meters	Secchi
Station Sampling Depth	meters	Sample Depth
Bottom Water Temperature	°C	BW Temp
Bottom Water Salinity	unitless	Salinity
Parameter	**Units**	**Database Field Name**
Bottom Water Dissolved Oxygen	mg L^{-1}	BW DO
Bottom Water NH_4 Concentration	µM	BW NH4
Bottom Water NO_2 Concentration	µM	BW NO2
Bottom Water NO_2 + NO_3 Concentration		BW NO2+NO3
Bottom Water PO_4 Concentration	µM	BW DIP
Sediment Redox Potential in Overlying Water (1 cm above sediment surface)	mV	EhOW
Sediment Redox Potential at Sediment Surface	mV	Eh0
Sediment Redox Potential at 1 cm below sediment surface	mV	Eh1
Sediment Redox Potential at 2 cm below sediment surface	mV	Eh2
% Surficial (top 1 cm) Sediment Carbon	% (weight)	PC
% Surficial (top 1 cm) Sediment Nitrogen	% (weight)	PN
% Surficial (top 1 cm) Sediment Phosphorus	% (weight)	PP
Sediment Total Surficial Chlorophyll Concentration	mg m^{-2}	Tot Chla
Sediment Active Surficial Chlorophyll Concentration	mg m^{-2}	Act Chla
Sediment Oxygen Consumption Rate	g O_2 m^{-2} day^{-1}	DO Flux
Sediment Dissolved Inorganic Phosphorus Flux Rate	µmoles P m^{-2} $hour^{-1}$	DIP Flux
Sediment Ammonium Flux Rate	µmoles N m^{-2} $hour^{-1}$	NH4
Sediment Nitrite Flux Rate	µmoles N m^{-2} $hour^{-1}$	NO2 Flux
Sediment Nitrite plus Nitrate Flux Rate	µmoles N m^{-2} $hour^{-1}$	NO2+NO3 Flux
Boynton or Non-Boynton Studies	Boynton or Other	Source

Only flux data generated using direct constituent measurement (rather than estimates from pore water profiles or modeling) were used for this review. Sediment exchange data were included from measurements made using either shipboard or laboratory mesocosm experiments (intact sediment cores incubated in a laboratory setting) or benthic chambers (domes or boxes placed on top of areas of sediment *in situ*). Only measurements made in the dark and under ambient conditions (e.g., water temperature, salinity) were used. Data were arranged according to individual reference and assigned an estuary name and corresponding source code.

Positive SOC fluxes were replaced with values of 0.00 in the main dataset. Raw values are still located in the individual spreadsheet files. Positive fluxes of dissolved oxygen in the dark are not possible under the measurement conditions included in this database. The data replaced is shown in Table 3-2 below.

Table 3-2. *Positive DO fluxes replaced in the database.*

Station	Date	Raw DO Flux
R-64	8/11/1994	0.020
R-78	6/1/1988	0.047
PNPT	8/17/1988	0.120
VIMSDeep	9/12/1990	0.127
EV1and2	1/19/1991	0.144
CHCL	8/11/1997	1.464

3-3. Flux Measurements

Flux rates for Boynton data were calculated using our standard methods for determining net sediment-water exchanges of nutrients (nitrogen and phosphorus) and oxygen (SONE). For data collected prior to 1996, a mean of replicate cores was used to better match Mini-SONE data (Boynton *et al.* 1997 (Interpretive Report #14)). Averages were also taken for Non-Boynton data when replicates were available. The protocols used in the Boynton data include a single sediment core with no blank. An intact sediment core constituted a benthic microcosm where changes in oxygen, nutrient and other compound concentrations were determined over a fixed incubation time. Oxygen and nutrient fluxes were estimated by calculating the rate of change in concentration over the incubation period and converting the volumetric rate to a flux using the volume to area ratio of each core. General calculations used in the Boynton data include:

Core Water Depth represents height of water above the sediment surface in the chamber.

$$Core\ H_2O\ Depth = (CORE\ VOL^{a}/CORE\ SURFACE\ AREA^{b})/100^{c}$$

Where

- *a* is the measured volume of water in the sediment core (ml)
- *b* is the surface area measurement of the core cylinder (cm^2)
- *c* converts measurement units to m

General method for calculating net sediment-water fluxes:

*NET DO FLUX ($gO_2\ m^{-2}\ d^{-1}$) = [(DO SLOPE) * (CORE H20 DEPTH^a) x (1440^b]*

NET NUTRIENT FLUX (μmoles-N $m^{-2}\ h^{-1}$) = [(VARIABLE SLOPE^c) x (Core H2O DEPTH^a) x (60^d) x (1000^e)]

Where

a	converts measurements from volumetric to areal basis
b	converts time units from per minute to per day and from mg to g
c	variables are NH_4^+, NO_2^-, NO_2^- + NO_3^- and DIP
d	converts time units from minutes to hours
e	converts concentration to moles

3-4. Parameter Decisions

In some cases, decisions were made on what data to include or how that data should be included to keep all data comparable (Table 3-3).

Table 3-3. *Dataset decision conditions.*

Item	**Explanation**
Water column blanks	Not included (no fluxes are blank corrected).
Flux core replicates	Average flux rate used.
Station Location	Where stations were sampled over multiple months, June (or summer) locations were used for each individual year of sampling.
Time	Where possible, times used are those that are as close to when the sediment core was collected as possible.
Item	**Explanation**
Sediment Chlorophyll	For sediments that are broken into a "surface" and 1 cm sample, the values from the 1 cm sample were used. Boynton data prior to 9/17/1985 were multiplied by 4 to account for loss of thin top layer.
Boynton and Kemp 1985	Used NO_3^- as NO_2^- + NO_3^- data.

3-5. Location and Frequency of Flux Measurements

Sampling locations included 290 individual stations throughout the Chesapeake Bay, its tributaries and Maryland's Coastal Bays (Figure 3-1). Stations on the map are coded to represent the type of sampling conducted. TMDL sampling (June, July and August of one year only) includes 138 of the stations (green squares on map). Yellow shaded areas denote Maryland watersheds with no data. At this time, we have not obtained additional datasets for the Choptank River.

There have been two agencies largely responsible for the creation of this data set. The first was the Maryland Biomonitoring program, a part of the Chesapeake Bay program. In this effort the measurement emphasis was on inter-annual scales of

variability at distinctive sites in the MD mainstem Bay and tributaries. The second, and more extensive effort, was supported by MDE wherein 20-30 sites were occupied three times per year in many tributary locations in the MD bay and MD coastal bays.

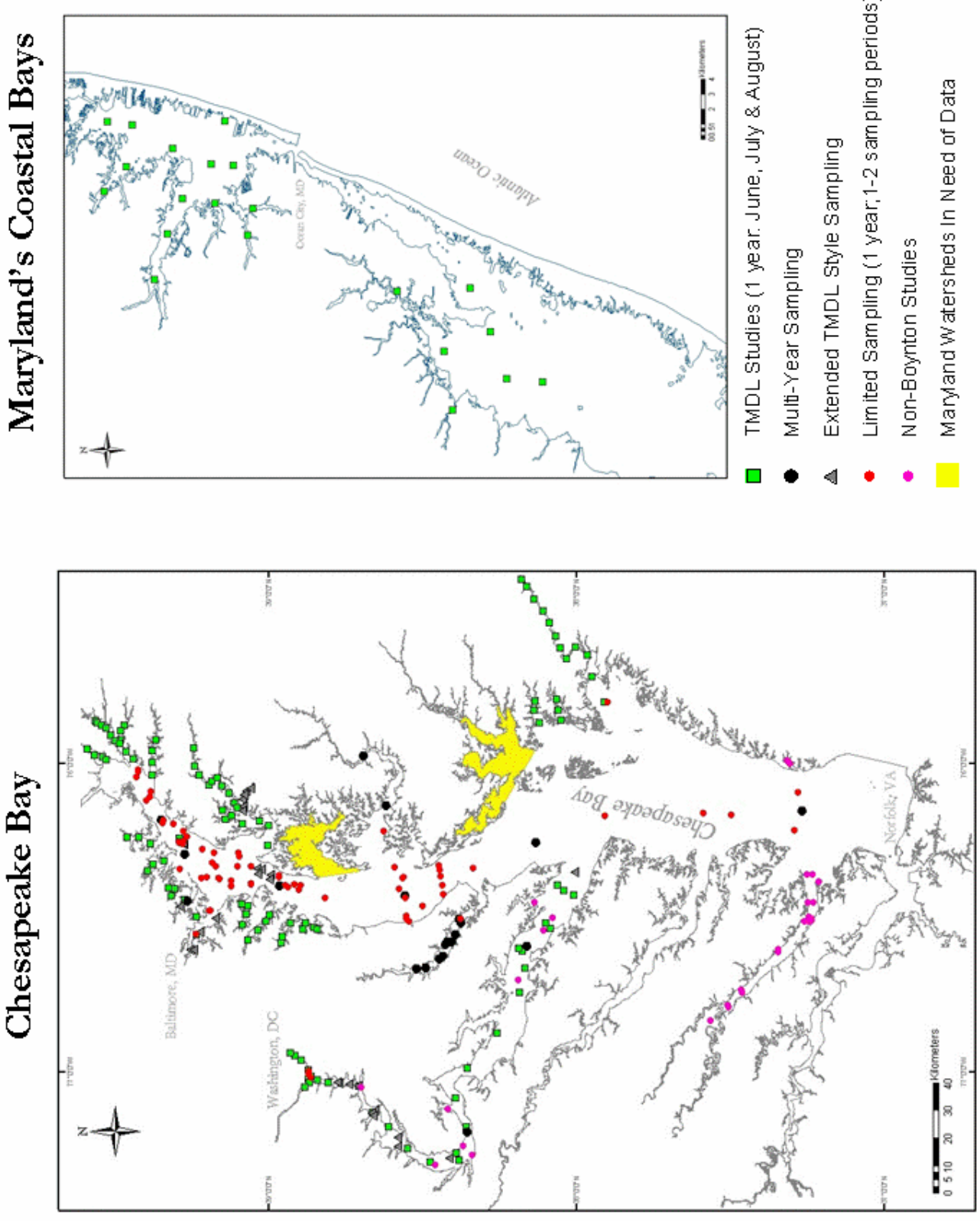

Figure 3-1. *Chesapeake Bay and Maryland's coastal bays sediment-water oxygen and nutrient flux measurement site locations.*

3-6. Data Management

Data for this synthesis was organized into spreadsheets (Microsoft Excel) in the following format (Figure 3-2).

Figure 3-2. *Example of data spreadsheets.*

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Station	Date	Time	Stat. Dpth	Secchi	Samp. Dpth	BW Temp	Salinity	BW DO	NH4	NO2	NO2+NO3	DIP	EhOW	EhO	Eh1
BU01	6/19/2005	9:54	3.4	0.4	3.0	25.1	2.50	11.10	2.30	0.32	10.80	0.07	285	288	209
BU01	7/24/2005	9:44	3.5	0.6	3.0	28.9	2.45	9.57	10.90	0.40	9.91	0.36	343	190	57
BU01	8/14/2005	9:38	3.1	0.6	3.0	29.9	3.12	6.48	8.29	0.38	8.27	0.08	306	114	101
BU02	6/7/2005	9:36	2.7	0.6	2.0	23.9	0.68	10.06	1.07	0.25	3.13	0.12	-123	-205	-199
BU02	7/19/2005	8:29	2.3	0.4	1.5	29.7	1.35	7.25	0.56	0.11	0.51	0.07	301	376	388
BU02	8/15/2005	7:51	2.1	0.4	2.0	30.4	1.58	6.76	0.21	0.16	0.36	0.10	350	268	224
BU03	6/7/2005	12:14	1.5	0.2	1.5	25.7	0.15	8.56	2.21	0.78	17.50	0.16	-20	-323	-329
BU03	7/19/2005	9:24	1.5	0.4	1.5	30.1	0.32	6.20	0.46	0.03	0.11	0.08	374	121	226
BU03	8/15/2005	8:43	1.2	0.4	1.0	30.4	0.73	6.69	0.21	0.12	0.18	0.15	281	151	119
GU01	6/19/2005	11:54	1.9	0.5	2.0	24.3	1.65	12.10	0.74	0.27	15.30	0.06	365	418	371
GU01	7/24/2005	11:21	2.5	0.8	2.5	28.5	3.80	9.12	7.05	0.17	11.90	0.12	381	361	363
GU01	8/14/2005	11:11	2.1	0.6	2.0	29.8	3.72	6.79	5.21	0.16	5.41	0.11	358	106	97
GU02	6/19/2005	13:03	1.7	0.4	1.5	24.9	0.83	12.20	1.60	0.43	19.30	0.06	346	332	111
GU02	7/24/2005	12:13	2.2	0.7	2.0	28.5	1.84	9.89	2.87	0.30	11.70	0.12	377	308	257
GU02	8/14/2005	12:04	1.9	0.7	1.5	30.5	2.00	8.15	0.29	0.15	0.34	0.08	348	88	95
GU03	6/7/2005	14:29	1.5	0.3	1.0	24.5	0.14	6.88	6.27	0.97	65.20	0.08	-115	-122	-170
GU03	7/19/2005	11:24	0.9	0.3	1.0	29.7	0.34	9.19	5.72	0.97	39.10	0.15	355	320	326
GU03	8/15/2005	10:23	0.9	0.6	0.5	30.7	1.35	6.78	1.86	0.24	1.50	0.09	209	94	82
MA01	6/8/2005	11:36	3.5	1.2	3.0	20.7	7.70	3.72	2.49	0.35	21.50	0.06	317	197	284
MA01	7/20/2005	10:19	2.9	0.8	2.5	29.4	8.39	7.50	10.55	0.24	3.98	0.05	386	41	89
MA01	8/16/2005	10:03	3.6	0.5	3.0	28.8	10.00	5.68	0.21	0.14	0.30	0.09	106	28	57
MA02	6/8/2005	10:44	4.3	1.2	4.0	20.4	8.49	4.00	4.20	0.51	24.40	0.06	151	169	173
MA02	7/20/2005	9:30	4.2	0.7	4.0	28.5	8.62	5.18	17.25	0.46	3.04	0.18	295	66	7
MA02	8/16/2005	9:19	4.2	0.5	4.0	28.2	10.54	0.63	15.86	0.59	0.70	0.82	202	71	54
MA03	6/8/2005	9:47	4.6	1.3	4.0	20.4	7.45	2.77	1.48	0.29	24.30	0.06	182	184	120
MA03	7/20/2005	8:36	4.7	0.8	4.0	28.2	8.36	3.92	17.16	0.30	2.71	0.43	211	114	26
MA03	8/16/2005	8:35	4.5	0.6	4.0	29.3	9.45	5.88	28.36	0.03	0.38	3.33	156	23	24
MA04	6/8/2005	8:23	4.8	1.1	4.0	19.4	7.21	1.02	0.75	0.41	13.60	0.08	132	96	166
MA04	7/20/2005	7:33	4.7	1.1	4.0	27.5	8.45	0.37	18.96	0.03	0.89	2.41	66	-203	-181
MA04	8/16/2005	7:35	4.5	0.8	4.0	28.1	9.38	0.71	51.14	0.02	1.64	6.21	40	-71	-109
MI01	6/13/2005	10:38	3.1	0.8	3.0	27.2	3.44	8.76	5.20	0.26	21.20	0.08	378	382	318
MI01	7/19/2005	15:24	2.9	0.9	2.5	29.6	3.99	6.95	9.38	0.12	6.54	0.31	374	228	0
MI01	8/15/2005	14:17	2.8	0.9	2.5	30.5	4.81	5.78	8.50	0.14	2.51	0.31	271	112	116
MI02	6/13/2005	9:52	2.0	0.6	2.0	27.9	2.07	9.87	1.82	0.33	12.10	0.06	358	18	-91
MI02	7/19/2005	14:44	1.5	0.5	1.5	30.6	3.23	8.21	4.01	0.09	0.39	0.10	-16	-44	28
MI02	8/15/2005	13:37	1.7	0.5	1.5	31.2	4.00	7.42	1.43	0.12	0.53	0.07	300	104	112
MI03	6/13/2005	8:57	2.4	0.5	2.0	27.7	1.81	10.35	5.00	0.47	9.08	0.06	320	208	-32
MI03	7/19/2005	13:56	2.1	0.4	2.0	29.6	3.44	7.26	3.17	0.07	1.03	0.09	89	57	69
MI03	8/15/2005	12:49	2.1	0.7	2.0	30.7	3.72	7.02	0.21	0.09	0.13	0.06	371	167	128
RH01	6/13/2005	15:02	2.0	0.9	2.0	28.2	8.41	9.67	2.99	0.16	2.55	0.10	390	402	290
RH01	7/21/2005	13:43	2.3	0.5	2.0	31.4	10.15	8.30					389	164	108
RH01	8/17/2005	14:12	2.1	0.4	2.0	29.8	11.64	9.80	0.21	0.04	0.22	0.18	180	124	83

When Non-Boynton data were entered, values were first entered as raw data taken from the publication (Figure 3-3) and then converted to the standard units and formatted as above (Figure 3-2). Boynton data was stored in a separate spreadsheet from non-Boynton data.

Raw Data from Reay et al. 1995 (Sediment-water column oxygen and nutrient fluxes in nearshore environments of the lower Delmarva Peninsula, USA (MEPS 118:215-22															
					umoles m-2 h-1					g O2 m-2 d-1		mg m-2 (top 1 cm)			
Station	Date	depth (m)	Water Temp(C)	Chamber Type	DO Flux	NH4Flux	NO3 Flux	NO2 Flux	DIPFlux	DO Flux	NO2+NO3 Flux		Tot.Chla	Act.Chla	
EV1and2	5/7/1990	1.0	23.6	dark	-2161.0	103.0	-2.0	1.0	-0.3	**-1.66**	-1.0		175	145	
EV1and2	7/17/1990	1.0	29.0	dark	-1704.0	101.0	1.0	-1.0	1.4	**-1.31**	0.0		140	130	
EV1and2	9/12/1990	1.0	26.0	dark	-949.0	62.0	0.0	-1.0	9.6	**-0.73**	-1.0		140	80	
EV1and2	1/19/1991	1.0	6.5	dark	188.0	30.0	12.0	-2.0	-1.1	**0.14**	10.0		210	125	
EV1and2	4/14/1991	1.0	14.5	dark	-18.0	43.0	-23.0	0.0	-1.5	**-0.01**	-23.0		160	90	
SC1and2	5/28/1990	1.0	19.0	dark	-2514.0	184.0	5.0	0.0	13.8	**-1.93**	5.0		60	45	
SC1and2	8/3/1990	1.0	29.7	dark	-3844.0	377.0	4.0	0.0	20.7	**-2.95**	4.0		110	60	
SC1and2	10/11/1990	1.0	24.7	dark	-1535.0	-4.0	-2.0	0.0	1.4	**-1.18**	-2.0		70	20	
SC1and2	2/10/1991	1.0	7.9	dark	-1596.0	76.0	-14.0	-1.0	2.2	**-1.23**	-15.0		85	55	
SC1and2	4/29/1991	1.0	23.8	dark	-1559.0	150.0	-12.0	-4.0	3.4	**-1.20**	-16.0		80	40	

Figure 3-3. *Example of raw Non-Boynton data spreadsheets.*

Station locations were stored in a spreadsheet and assigned to a tributary (Table 3-4). Latitude and longitude were expressed as decimal degrees (Datum NAD 83).

Table 3-4. *Station locations and tributary assignments.*

Station	Latitude	Longitude	Tributary
AN01	38.8613	-77.0142	Anacostia
ANA-24	38.8635	-77.0162	Anacostia
AN02	38.8696	-76.9929	Anacostia
ANA-21	38.8713	-77.0097	Anacostia
ANA-19	38.8720	-76.9978	Anacostia
AN03	38.8952	-76.9618	Anacostia
AN04	38.9153	-76.9472	Anacostia
AN05	38.9279	-76.9392	Anacostia
WCPT	39.2627	-76.4441	Back
MDGT	39.2710	-76.4420	Back
DPCK	39.2862	-76.4621	Back
BA01	38.0500	-75.8583	Big Annemessex
BA02	38.0583	-75.8250	Big Annemessex
BA03	38.0667	-75.7900	Big Annemessex
BM01	39.4691	-75.8753	Bohemia
BM03	39.4780	-75.9222	Bohemia
BM02	39.4801	-75.8939	Bohemia
BU01	39.3828	-76.2602	Bush
BU02	39.4195	-76.2393	Bush
BU03	39.4583	-76.2375	Bush
SC1and2	37.3100	-76.0000	Cherrystone Inlet
EV1and2	37.3200	-75.9900	Cherrystone Inlet
CR19	38.9989	-76.2016	Chester
CR20	39.0037	-76.2639	Chester
CR18	39.0285	-76.1849	Chester
CR17	39.0833	-76.1955	Chester
CR16	39.1031	-76.1421	Chester
CR09	39.1100	-76.1277	Chester
CR15	39.1192	-76.1679	Chester
CR08	39.1282	-76.0966	Chester
CR14	39.1404	-76.1808	Chester
CR13	39.1474	-76.1494	Chester
CR07	39.1528	-76.0720	Chester

CR06	39.1652	-76.0459	Chester
CR05	39.1840	-76.0581	Chester
CR04	39.1935	-76.0681	Chester
CR03	39.2238	-76.0353	Chester
CR02	39.2391	-76.0080	Chester
CR01	39.2420	-75.9482	Chester
HNPT	38.6202	-76.1335	Choptank
T2	38.6272	-76.2167	Choptank
WDHL	38.6908	-75.9717	Choptank
CRa	39.0572	-76.0769	Corsica
CR10	39.0738	-76.0870	Corsica
CRb	39.0786	-76.0979	Corsica
CR12	39.0811	-76.1358	Corsica
CR11	39.0831	-76.1127	Corsica
CRc	39.0848	-76.1498	Corsica
EK09	39.4372	-75.9841	Elk
EK08	39.4617	-75.9602	Elk
EK07	39.4824	-75.9355	Elk
EK06	39.4975	-75.9250	Elk
EK05	39.5111	-75.9067	Elk
EK04	39.5273	-75.8836	Elk
EK03	39.5402	-75.8752	Elk
EK02	39.5543	-75.8680	Elk
EK01	39.5612	-75.8622	Elk
GU01	39.3389	-76.3139	Gunpowder
GU02	39.3750	-76.3250	Gunpowder
GU03	39.3905	-76.3473	Gunpowder
MA02	39.0681	-76.4597	Magothy
MA03	39.0734	-76.4875	Magothy
MA04	39.0853	-76.5229	Magothy
MA01	39.0865	-76.4542	Magothy
YKST	37.2687	-76.1505	Mainstem
CPCH	37.2833	-76.0917	Mainstem
NPCT	37.2955	-76.2148	Mainstem
B5	37.5000	-76.1667	Mainstem
RPST	37.5900	-76.1610	Mainstem
SMPT	37.9117	-76.1685	Mainstem
104-D1	38.0068	-76.3492	Mainstem
PNPT	38.1332	-76.2522	Mainstem
PRBY	38.3367	-76.3367	Mainstem
MB12	38.4333	-76.4237	Mainstem
MB13	38.4382	-76.3925	Mainstem
MB14	38.4417	-76.3658	Mainstem
MB15	38.4475	-76.3450	Mainstem
MB16	38.4492	-76.3308	Mainstem
B3	38.5022	-76.4597	Mainstem
PKCK	38.5462	-76.5098	Mainstem
MB07	38.5535	-76.5032	Mainstem
MB08	38.5549	-76.4940	Mainstem
MB09	38.5563	-76.4342	Mainstem
R-64	38.5586	-76.4264	Mainstem
MB11	38.5632	-76.3672	Mainstem
MB10	38.5651	-76.3710	Mainstem

B4	38.5772	-76.4042	Mainstem
TPBY	38.5920	-76.3365	Mainstem
BDPT	38.8167	-76.4333	Mainstem
DT-1	38.8977	-76.3933	Mainstem
TMPT	38.9013	-76.4077	Mainstem
DT-4	38.9160	-76.3912	Mainstem
DT-7	38.9385	-76.3988	Mainstem
DT-10	38.9458	-76.3940	Mainstem
R-78	38.9635	-76.3937	Mainstem
UB17	38.9667	-76.3612	Mainstem
UB16	38.9667	-76.3667	Mainstem
104-D2	38.9938	-76.3583	Mainstem
104-DR	38.9952	-76.3727	Mainstem
104-S2	39.0240	-76.3425	Mainstem
104-SR	39.0342	-76.3554	Mainstem
104-S1	39.0372	-76.3388	Mainstem
UB15	39.0567	-76.3333	Mainstem
CHCL	39.0585	-76.3916	Mainstem
CHSL	39.0585	-76.3868	Mainstem
DC07	39.0950	-76.3000	Mainstem
UB14	39.0978	-76.2880	Mainstem
UB13	39.1017	-76.3333	Mainstem
DC06	39.1216	-76.3966	Mainstem
UB12	39.1217	-76.3800	Mainstem
BECL	39.1598	-76.3724	Mainstem
BESL	39.1621	-76.3710	Mainstem
UB11	39.1717	-76.3333	Mainstem
DC04	39.1779	-76.2885	Mainstem
UB10	39.1850	-76.3200	Mainstem
B2	39.2000	-76.3672	Mainstem
HTMR	39.2000	-76.3667	Mainstem
UB09	39.2155	-76.2778	Mainstem
UB08	39.2203	-76.3715	Mainstem
TCCL	39.2646	-76.2363	Mainstem
NACL	39.2646	-76.2363	Mainstem
PLIS	39.2713	-76.2903	Mainstem
GCNT	39.2755	-76.2603	Mainstem
UB07	39.2777	-76.2190	Mainstem
GC-2	39.2783	-76.2537	Mainstem
GW-3	39.2788	-76.2560	Mainstem
GE-1	39.2791	-76.2550	Mainstem
GC-1	39.2798	-76.2535	Mainstem
GW-1	39.2798	-76.2585	Mainstem
92-1	39.2836	-76.2450	Mainstem
GW-2	39.2863	-76.2500	Mainstem
GE-2	39.2864	-76.2522	Mainstem
92-2	39.2895	-76.2414	Mainstem
UB06	39.2895	-76.3413	Mainstem
GTST	39.2917	-76.2527	Mainstem
GWST	39.2925	-76.2518	Mainstem
B1	39.3083	-76.1950	Mainstem
WNCK	39.3083	-76.1950	Mainstem
DC03	39.3417	-76.1833	Mainstem

UB05	39.3450	-76.1917	Mainstem
SLPD	39.3478	-76.1812	Mainstem
DC02	39.3833	-76.0900	Mainstem
UB04	39.3867	-76.1067	Mainstem
UB03	39.3975	-76.1183	Mainstem
DC01	39.4246	-76.0187	Mainstem
UB02	39.4250	-76.0250	Mainstem
UB01	39.4283	-76.0433	Mainstem
MN03	38.1217	-75.8667	Manokin
MN01	38.1367	-75.7967	Manokin
MN02	38.1383	-75.8250	Manokin
NB01	38.1786	-75.2335	MD Coastal Bays
NB02	38.2001	-75.2317	MD Coastal Bays
NB04	38.2099	-75.2036	MD Coastal Bays
SP04	38.2223	-75.1775	MD Coastal Bays
MC01	38.2327	-75.2503	MD Coastal Bays
NB03	38.2376	-75.2152	MD Coastal Bays
TC01	38.2659	-75.1792	MD Coastal Bays
IW07	38.3521	-75.1299	MD Coastal Bays
IW08	38.3552	-75.1458	MD Coastal Bays
IW09	38.3639	-75.1041	MD Coastal Bays
IW04	38.3690	-75.0774	MD Coastal Bays
IW06	38.3750	-75.1264	MD Coastal Bays
IW01	38.3774	-75.1030	MD Coastal Bays
IW05	38.3943	-75.1238	MD Coastal Bays
AS06	38.4004	-75.0937	MD Coastal Bays
IW03	38.4035	-75.1449	MD Coastal Bays
IW02	38.4113	-75.1723	MD Coastal Bays
AS02	38.4245	-75.0797	MD Coastal Bays
AS05	38.4280	-75.1046	MD Coastal Bays
AS03	38.4393	-75.0777	MD Coastal Bays
AS04	38.4415	-75.1194	MD Coastal Bays
MI01	39.3048	-76.4042	Middle
MI03	39.3151	-76.4302	Middle
MI02	39.3236	-76.4028	Middle
NR04	39.5252	-75.9856	Northeast
NR03	39.5388	-75.9775	Northeast
NR02	39.5643	-75.9731	Northeast
NR01	39.5874	-75.9530	Northeast
CTBY	39.1727	-76.5000	Patapsco
BWCL	39.1910	-76.4766	Patapsco
BWSL	39.1939	-76.4752	Patapsco
RVBH	39.2230	-76.5417	Patapsco
HMCK	39.2324	-76.4965	Patapsco
FFOF	39.2338	-76.5543	Patapsco
FMCL	39.2371	-76.5510	Patapsco
INHB	39.2748	-76.6027	Patapsco
FYBR	39.2540	-76.6027	Patapsco
PX32	38.3763	-76.5127	Patuxent
PX33	38.3763	-76.5127	Patuxent
T1	38.3783	-76.5028	Patuxent
STLC	38.3803	-76.5011	Patuxent
BRIS	38.3933	-76.5511	Patuxent

PX23	38.4048	-76.5743	Patuxent
PX25	38.4198	-76.5760	Patuxent
PX21	38.4250	-76.5850	Patuxent
PX15	38.4338	-76.6220	Patuxent
MRPT	38.4461	-76.6317	Patuxent
PX07	38.4895	-76.6588	Patuxent
BUVA	38.5185	-76.6637	Patuxent
T3	37.9006	-75.7992	Pocomoke
PS01	37.9100	-75.8000	Pocomoke
PS02	37.9500	-75.7167	Pocomoke
PC10	37.9650	-75.6483	Pocomoke
PC09	38.0033	-75.6200	Pocomoke
PC08	38.0333	-75.6600	Pocomoke
PC07	38.0550	-75.6233	Pocomoke
PC06	38.0683	-75.5867	Pocomoke
PC05	38.0883	-75.5417	Pocomoke
PC04	38.1100	-75.5033	Pocomoke
PC03	38.1400	-75.4667	Pocomoke
PC02	38.1617	-75.4250	Pocomoke
PC01	38.1783	-75.4000	Pocomoke
PT01	38.0097	-76.4249	Potomac
PT02	38.0415	-76.4125	Potomac
PT03	38.0613	-76.3927	Potomac
V-3	38.0800	-76.5000	Potomac
PT04	38.0846	-76.5328	Potomac
PT05	38.1014	-76.5167	Potomac
V-PP	38.1100	-76.5400	Potomac
V-SM	38.1400	-76.4500	Potomac
RGPT	38.1622	-76.5893	Potomac
PT08	38.1681	-76.6635	Potomac
PT06	38.1774	-76.6082	Potomac
PT09	38.1864	-76.7408	Potomac
PT07	38.1890	-76.5974	Potomac
V-BB	38.1900	-76.7000	Potomac
PT10	38.2583	-76.8736	Potomac
V-PC	38.3400	-77.2700	Potomac
PT11	38.3555	-76.9889	Potomac
MDPT	38.3562	-77.1915	Potomac
PT13	38.3572	-77.1773	Potomac
V-16	38.3700	-77.2400	Potomac
PT14	38.3831	-77.2864	Potomac
PT15	38.3904	-77.2622	Potomac
PT12	38.3930	-77.0856	Potomac
Eight	38.4136	-77.2765	Potomac
V-PT	38.4200	-77.1200	Potomac
V-Q	38.4600	-77.3000	Potomac
PT16	38.4741	-77.2917	Potomac
PT17	38.5489	-77.2485	Potomac
Seven	38.5805	-77.2118	Potomac
Six	38.5821	-77.2388	Potomac
PT18	38.6113	-77.1775	Potomac
Five	38.6538	-77.1240	Potomac
GNCV	38.6592	-77.1400	Potomac

PT19	38.6640	-77.1307	Potomac
Four	38.6665	-77.1320	Potomac
V-26	38.7000	-77.0500	Potomac
PT20	38.7077	-77.0469	Potomac
Three	38.7108	-77.0423	Potomac
HGNK	38.7390	-77.0392	Potomac
One	38.7705	-77.0338	Potomac
Two	38.7781	-77.0333	Potomac
PT21	38.8054	-77.0336	Potomac
PT22	38.8423	-77.0268	Potomac
PT24	38.8679	-77.0334	Potomac
PT23	38.8708	-77.0217	Potomac
PT25	38.8832	-77.0493	Potomac
RH01	38.8797	-76.5176	Rhode
RH02	38.8870	-76.5375	Rhode
SF01	39.3663	-75.9225	Sassafras
SF02	39.3756	-75.9575	Sassafras
SF03	39.3780	-75.9954	Sassafras
SF04	39.3780	-76.0353	Sassafras
SE01	38.9957	-76.4902	Severn
SE02	39.0094	-76.5108	Severn
SE03	39.0355	-76.5400	Severn
SE04	39.0679	-76.5729	Severn
SO01	38.9288	-76.5180	South
SO02	38.9542	-76.5611	South
SO03	38.9580	-76.5799	South
WE02	38.8403	-76.5361	West
WE01	38.8516	-76.5310	West
YKSS	37.2500	-76.5100	York
Sweet Hall	37.5667	-76.8333	York
Goodwin Islands	37.2167	-76.3833	York
VIMS Shoal	37.2483	-76.4965	York
Claybank SH	37.3242	-76.5900	York
Claybank Deep	37.3242	-76.5933	York
Mumfort Island	37.2622	-76.5109	York
VIMS Deep	37.2408	-76.4863	York
YR	37.2687	-76.1530	York
YR Mouth Deep	37.2555	-76.3530	York
York Mouth	37.2554	-76.3572	York
PRPR Deep	37.4275	-76.7002	York
PRPR Shoal	37.4300	-76.7000	York
LE4CH	37.2340	-76.4498	York
LE4SH	37.2513	-76.4505	York
RET4CH	37.5094	-76.7897	York
RET4SH	37.5114	-76.7817	York

3-7. Database Design

A database titled "Chesapeake Bay Flux Synthesis Database" was created in Microsoft Access 2003 from three spreadsheets: Boynton Data, Non-Boynton data and Station Locations. Two tables were created:

Flux Synthesis Data

Flux Synthesis Station Locations

A form was created to facilitate querying the database (Figure 3-4). It allows the user to construct multiple parameter queries and exports desired data to a Microsoft Excel spreadsheet (Figure 3-5).

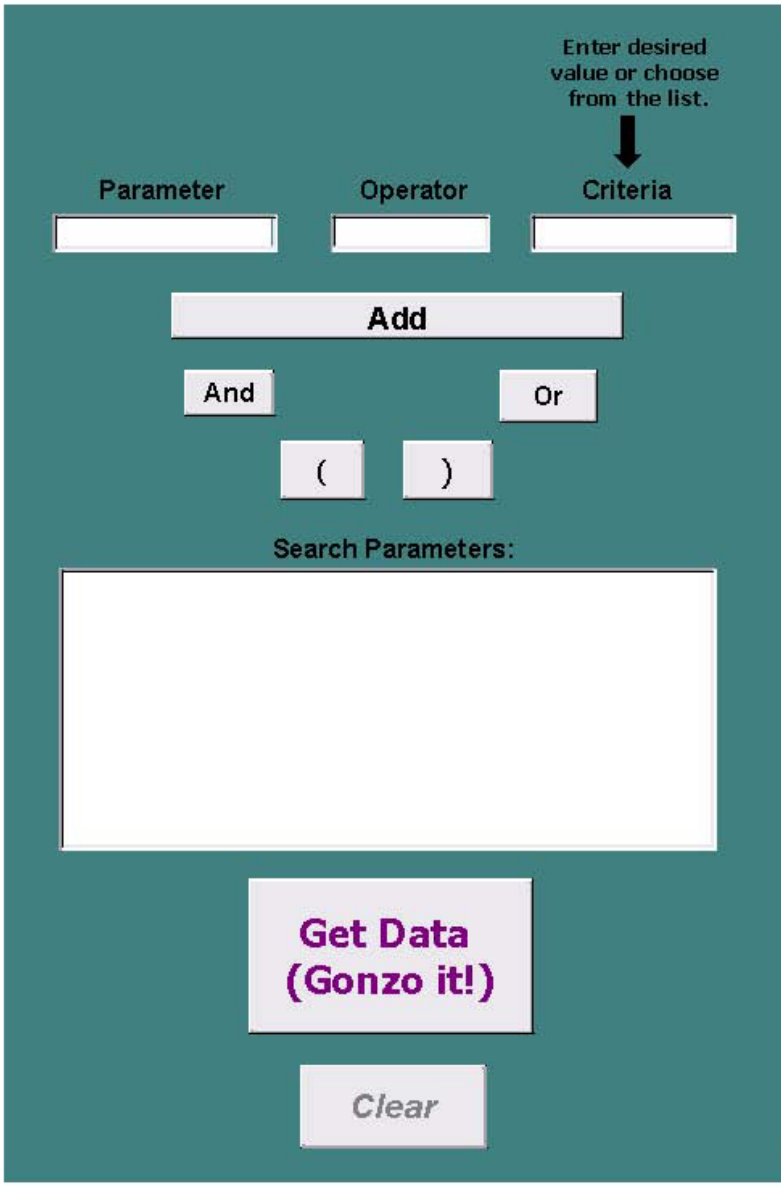

Figure 3-4. *Database form created as interface for queries.*

Tributary:	Longitude:	Latitude:	Station:	Date:	Time:	Station Depth:	Secchi:	Sample Depth:	BW Temp:
Mainstem	-76.195	39.30833333	WNCK	30-Jul-80	0.493055556	4		3.5	28.1
Mainstem	-76.36666667	39.2	HTMR	07-May-81	0.708333333	4		3.5	14
Mainstem	-76.195	39.30833333	B1	07-May-81	0.361111111	4	0.4	3.5	14
Mainstem	-76.29033333	39.27133333	PLIS	17-Apr-88	0.725694444	3.4	0.4	3	11.1
Mainstem	-76.29033333	39.27133333	PLIS	28-Jul-98	0.384027778	4.5	0.4	3	26.45
Mainstem	-76.25	39.28633333	GW-2	14-Jun-94	0.743055556	4	0.4	3.5	25.1
Mainstem	-76.29033333	39.27133333	PLIS	18-Jul-96	0.583333333	3.3	0.5	2.5	26.9
Mainstem	-76.29033333	39.27133333	PLIS	12-Jun-96	0.350694444	4.2	0.5	3	23.9
Mainstem	-76.29033333	39.27133333	PLIS	13-Jun-95	0.733333333	3.6	0.6	3	22.6
Mainstem	-76.25	39.28633333	GW-2	14-Jun-95	0.348611111	4.8	0.6	4	22
Mainstem	-76.25	39.28633333	GW-2	18-Jul-94	0.495138889	4.5	0.6	4	28.5
Mainstem	-76.195	39.30833333	B1	01-Aug-80	0.493055556	4	0.6	3.5	28.2
Mainstem	-76.29033333	39.27133333	PLIS	16-Aug-96	0.322916667	3.9	0.6	3	25.1
Mainstem	-76.25	39.28633333	GW-2	18-Jul-96	0.354166667	4.5	0.6	4	26.5
Mainstem	-76.36722222	39.2	B2	01-Aug-80	0.291666667	4.6	0.7	4.1	27.2
Mainstem	-76.36722222	39.2	B2	07-May-81	0.578472222	4.6	0.7	4.1	14.4
Mainstem	-76.34133	39.2895	UB06	28-Jul-98	0.329861111	4.5	0.7	4	26.7
Mainstem	-76.29033333	39.27133333	PLIS	15-Aug-88	0.720833333	4	0.7	3	30.1
Mainstem	-76.29033333	39.27133333	PLIS	18-Jul-94	0.709027778	3.9	0.7	3	28.6
Mainstem	-76.29033333	39.27133333	PLIS	12-Aug-94	0.440972222	4	0.7	3	25.6
Mainstem	-76.25	39.28633333	GW-2	10-Jul-95	0.564583333	4.5	0.7	4	25.5
Mainstem	-76.25366667	39.27833333	GC-2	19-Aug-93	0.375	4.5	0.8	4	26.7
Mainstem	-76.11833	39.3975	UB03	27-Jul-98	0.541666667	4	0.8	3.5	27.8
Mainstem	-76.25	39.28633333	GW-2	17-Jul-97	0.40625	4.5	0.9	4	28.4
Mainstem	-76.25	39.28633333	GW-2	12-Aug-94	0.384027778	4.3	0.9	3	25.7
Mainstem	-76.25	39.28633333	GW-2	29-Aug-95	0.409722222	4.5	0.9	4	25.8
Mainstem	-76.25	39.28633333	GW-2	12-Jun-97	0.438888889	4	0.9	3.5	20.7
Mainstem	-76.29033333	39.27133333	PLIS	15-Jun-94	0.359722222	3	0.9	2.5	24.8
Mainstem	-76.25	39.28633333	GW-2	14-Aug-97	0.392361111	4.2	1	3	26.3
Mainstem	-76.29033333	39.27133333	PLIS	14-Jul-92	0.6875	3.5	1	3	27.3
Mainstem	-76.29033333	39.27133333	PLIS	11-Jul-95	0.568055556	3	1	2.5	25.9
Mainstem	-76.29033333	39.27133333	PLIS	18-Aug-93	0.534722222	3.5	1.1	3	27.1
Mainstem	-76.29033333	39.27133333	PLIS	14-Jun-93	0.657638889	3.5	1.1	3	23.5
Mainstem	-76.29033333	39.27133333	PLIS	12-Jun-97	0.336805556	3.5	1.1	3	20.6
Mainstem	-76.29033333	39.27133333	PLIS	22-Jul-93	0.35625	3.5	1.2	3	26.2
Mainstem	-76.2535	39.27983333	GC-1	18-Aug-93	0.473611111	3.5	1.3	3	26.8
Mainstem	-76.29033333	39.27133333	PLIS	17-Jul-97	0.322916667	3.9	1.3	3	28.6
Mainstem	-76.29033333	39.27133333	PLIS	10-Aug-92	0.666666667	3	1.4	2.5	25.9
Mainstem	-76.29033333	39.27133333	PLIS	28-Aug-95	0.743055556	3	1.5	2.5	26.4
Mainstem	-76.33083333	38.44916667	MB16	06-Jul-98	0.647222222	3	1.6	2.5	26.36
Mainstem	-76.29033333	39.27133333	PLIS	14-Aug-97	0.317361111	3.9	1.9	3	26.5
Mainstem	-76.29033333	39.27133333	PLIS	04-Nov-88	0.319444444	3	2.6	2.5	9.8

Figure 3-5. *Example of a portion of the Excel table generated as query output from the following search parameters:*
[Tributary] = "Mainstem" And [Station Depth] < 5 from the Flux Synthesis database.

Additional data can be added to this database provided it is in the formats described above.

3-8. Data Source References and Literature Cited

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Chapter 4

Broad Characterization of Chesapeake Bay Sediment Flux Data

4-1. Background

In this section we present, describe and interpret broad characterizations of sediment flux data and associated environmental variables based on all observations made in the Bay region. This is the broad brush assessment of sediment nutrient and oxygen fluxes and associated variables. We have divided this section into four units including physical, chemical and biological variables known to influence sediment flux characteristics, the flux measurements and a series of summary conclusions. This broad characterization will be especially useful in comparing and contrasting results from specific areas within the Bay system.

4-2. Physical Variables

Measurements of sediment fluxes were conducted at 289 different sites and 1520 station depths were recorded (many stations were occupied repeatedly).

Sediment fluxes were made at depths that encompassed virtually the entire depth distribution of important Bay habitats. Station depths ranged from about 1 to 42 m; the median station depth was about 6m (Table 4-1; Fig. 4-1). The majority of measurements (60%) were made in waters <8 m in depth. It was an appropriate decision to favor shallow sites for flux measurements because the influence of sediment processes is inversely proportional to water depth (see Chapter 7). Secchi depths ranged from about 0.1 to 5.0 m based on a total sample of 1409 measurements. The median value was 1.0 m (Table 4-1; Fig. 4-1). With a median Secchi disk depth on 1.0 m the depth of 1% light penetration is approximately 2.7 m. Thus, with a median depth of 6 m and Secchi depth on 1.0 m the vast majority of sediments sampled were aphotic. In addition, all sediment core incubations were conducted under dark conditions. Hence, these fluxes represent processes associated with aphotic sediments. Bottom water temperature ranged from 4 to 31 °C, a very large range. However, the median temperature at the time of flux measurements was 25 °C and this indicates that the majority of fluxes were conducted under temperature conditions above the annual average temperature (Table 4-1; Figure 4-1). About 80% of all fluxes were made at >20 °C. However, previous work (Boynton et al 1980) clearly indicated that the sediment processes routinely measured in monitoring programs were highest at temperatures > 20 °C. Thus, effort was expended during the warmer portions of the year.

4-3. Chemical and Biological Variables

Bottom water salinity ranged from 0.0 to 30, again encompassing the full range of salinities encountered in the Chesapeake Bay and Maryland Coastal Bays. The median salinity value was about 11, representing low mesohaline conditions (Table 4-1; Fig. 4-2). Bottom water dissolved oxygen concentrations ranged from 0.0 to 17 mg l^{-1} and the median value was about 6 mg l^{-1}. The median value for DO indicates that most sediment fluxes were made under normoxic conditions, at least at the time of measurement. However, there were a substantial number of flux measurements made under hypoxic/near-anoxic conditions (31% at DO < 4 mg l^{-1}; Table 4-1; Fig. 4-2) and this is

important because of the strong effect DO conditions have on the pattern and magnitude of flux (see Chapters 8 and 11). Bottom water ammonium concentrations exhibited a huge range (0.02 to 112 µM) and this was not expected. It seems that we had become accustomed to surface water ammonium concentrations which are often very low (<1 µM) especially during summer periods. However, even the median value of 5.0 µM for ammonium indicates the importance of sediments as a source of recycled ammonium (Table 4-1; Fig. 4-2). Bottom water nitrite and nitrate plus nitrite concentrations ranged from 0.01 - 27.0 and from 0.01 - 207 µM, respectively. Most elevated nitrite concentrations occurred during fall periods and are thought to be generated by incomplete sediment nitrification. The very large range in nitrate concentration reflect the important influence of rivers draining the Chesapeake watershed and, as we will show later, have a strong effect on sediment nitrate plus nitrite fluxes (Table 4-1; Figure 4-2; see Chapter 4). Bottom water phosphorus concentrations ranged from 0.02 to 13 µM with a median value of about 1.0 µM. As with ammonium, deep water concentrations of DIP were elevated compared to surface water values and again emphasizes the importance of sediments as a recycled source of this essential element.

Table 4-1. *Site characteristics for the sediment water flux database.*

Variable	Median	Range	N
Stations			289
Water Depth (m)	6	1 to 42	1530
Secchi Depth (m)	1	0.1 to 5	1409
Bottom Water Temperature (°C)	25	4 to 31	1516
Bottom Water Salinity	11	0 to 30	1505
Bottom Water Dissolved Oxygen (mg L^{-1})	6	0 to 17	1482
Bottom Water NH_4 (µM)	5	0.02 to 112	1483
Bottom Water NO_2 (µM)	0	0.01 to 27	1363
Bottom Water NO_2 + NO_3 (µM)	4	0.01 to 207	1487
Bottom Water PO_4 (µM)	1	0.02 to 13	1492
Overlying Water Eh (Corrected mV)	353	-264 to 458	1347
Sediment Surface Eh (Corrected mV)	307	-323 to 462	1331
Sediment Eh @ 1 cm (Corrected mV)	177	-329 to 539	1360
Sediment Eh @ 2 cm (Corrected mV)	140	-325 to 502	1350
Surficial Sediment Particulate Carbon (%wt)	3	0.03 to 22	1430
Surficial Sediment Particulate Nitrogen (%wt)	0.3	0.01 to 1	1370
Surficial Sediment Particulate Phosphorus (%wt)	0.1	0.001 to 1	1352
Surficial Sediment Total Chlorophyll-*a* (mg m^{-2})	72	4 to 541	1395
Surficial Sediment Active Chlorophyll-*a* (mg m^{-2})	21	1 to 441	1367
Sediment Oxygen Consumption (g O_2 m^{-2} d^{-1})	1.0	0.003 to 7	1509
Sediment DIP Flux (µmoles P m^{-2} h^{-1})	6	-137 to 229	1480
Sediment Flux NH_4 (µmoles N m^{-2} h^{-1})	193	-148 to 2169	1495
Sediment Flux NO_2 (µmoles N m^{-2} h^{-1})	0	-138 to 129	1232
Sediment Flux NO_2 + NO_3 (µmoles N m^{-2} h^{-1})	0	-607 to 288	1490
Surface Water Respiration (g O_2 m^{-3} d^{-1})	2.0	0.1 to 13	186

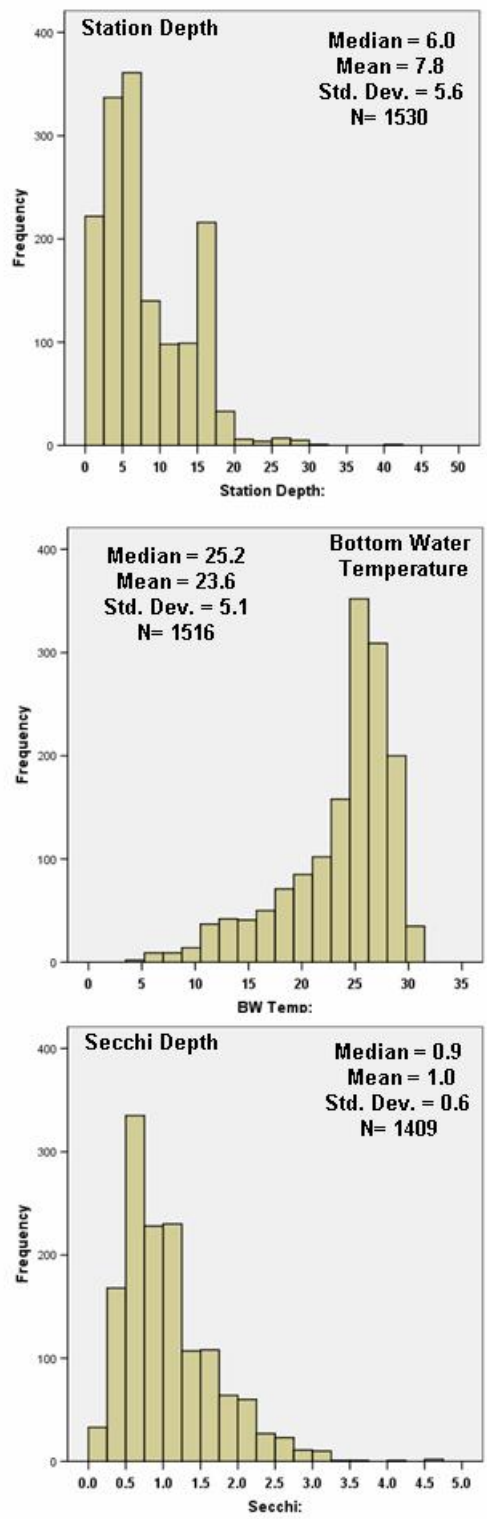

Figure 4-1. *Variable frequency histograms for water depth (m), bottom water temperature (°C) and secchi depth (m) for the sediment flux database.*

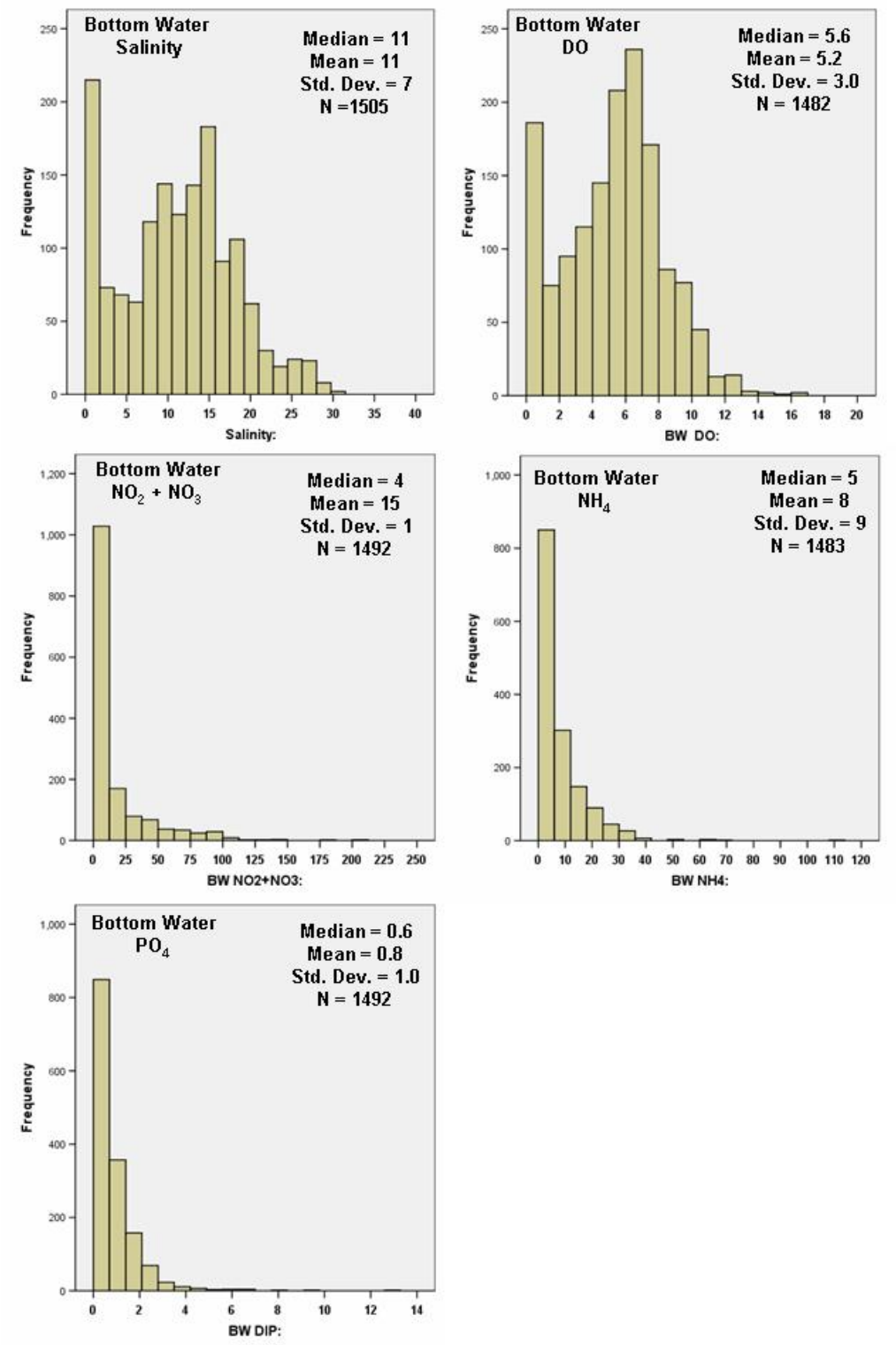

Figure 4-2. *Frequency histograms of bottom water conditions: salinity, DO (mg L^{-1}), NO_2+NO_3 (µM), NH_4 (µM) and PO_4 (µM) for the sediment flux database.*

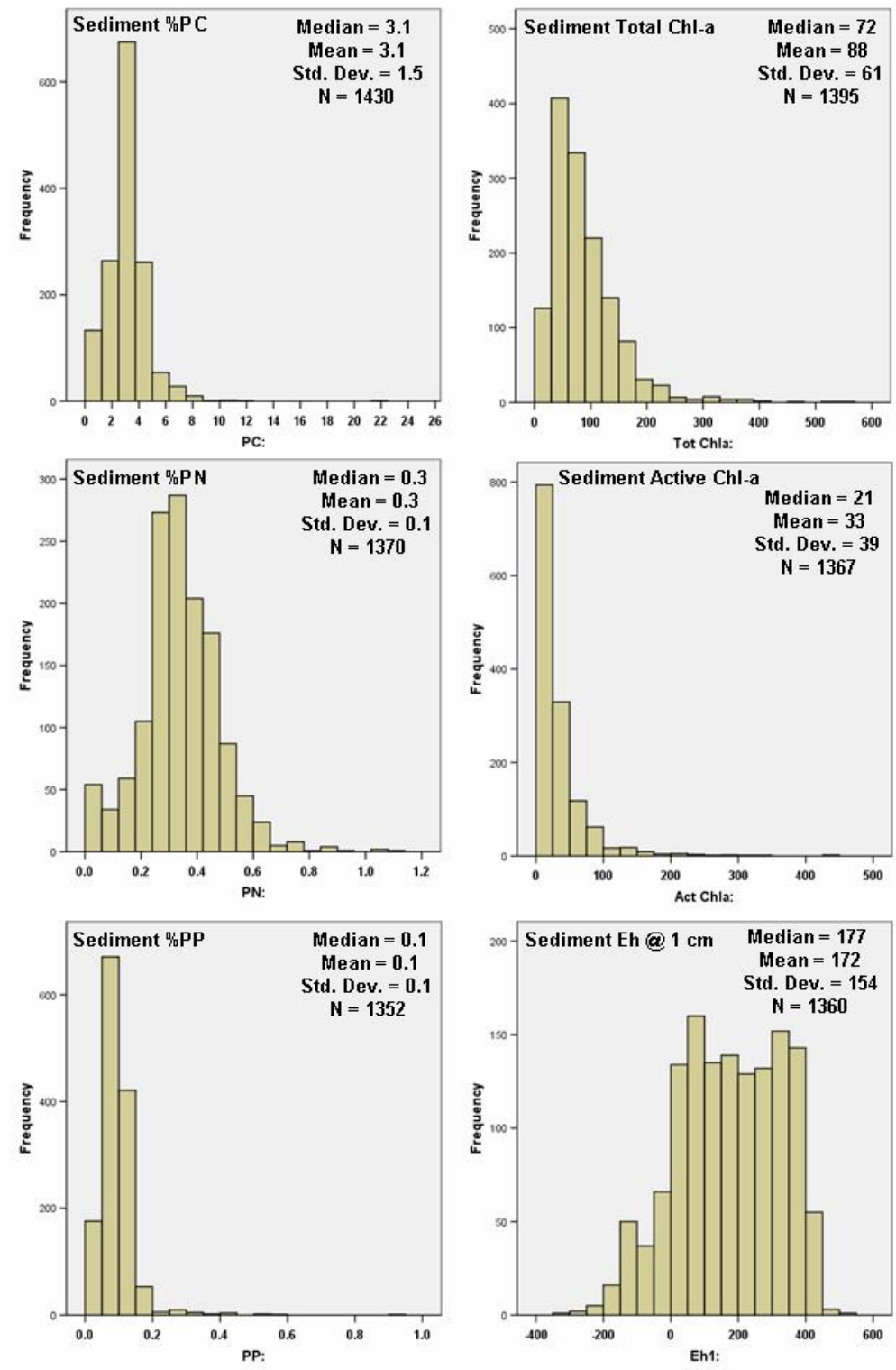

Figure 4-3. *Frequency histograms of sediment conditions: surficial (top 1 cm) particulate carbon (%), particulate N (%), particulate P (%), total and active chlorophyll-a (mg m^{-2}) and Eh at 1 cm (mV) for the sediment flux database.*

There were five different sediment variables measured at almost all sediment flux sites and these included sediment Eh (to estimate the redox condition of sediments; these measurements were made at various depths in the sediment column), sediment particulate carbon (PC), particulate nitrogen (PN) and particulate phosphorus (PP) to obtain an estimate of total sediment reserves, and two measures of labile organic matter at the sediment surface (total and active chlorophyll-a). Sediment Eh at one centimeter below the sediment surface ranged from -329 mV (very reduced sediments) to 539 (very oxidized sediments) with a median value of 177 mV (Table 4-1; Fig. 4-3). This extreme range proved to be useful because sediment redox conditions have a strong influence on sediment processes. Surficial sediment PC, PN and PP concentrations ranged from 0.03 to 22%, 0.01 to 1.0 and 0.001 to 1.0, respectively, with median values of 3.0, 0.3 and 0.1 % weight of dry sediments. Median values are typical of estuarine sediments (Boynton et al 1995). Surficial sediment active and total chlorophyll-a values ranged from 1 to 441 and 4 to 541 mg m^{-2}, with medians of 21 and 72, respectively. For the most part, the surficial sediment chlorophyll-a values are biased towards summer values which are generally lower than late winter-spring or even fall values. We do have spring and fall measurements but they represent only about 28% of all observations. There are several reasons for this pattern. First, it appears that a large percentage of both the spring and fall diatom blooms reach the sediment surface more or less intact. Thus, there is a bigger vertical flux of chlorophyll-a during these seasons than during summer when more of the phytoplankton biomass in the water column is grazed or completely metabolized by bacteria and other small heterotrophs before reaching the bottom. Second, chlorophyll-a degrades as a function of temperature (Hagy et al 2005) and the cooler bottom temperatures of spring "preserve" chlorophyll-a longer than during summer. As we will show later (see Chapter 6) it is unfortunate that spring sediment sampling for chlorophyll-a was not a part of most sediment flux monitoring programs.

4-4. Sediment Oxygen and Nutrient Fluxes

There were five sediment flux measurements routinely made in most of the sediment flux monitoring programs reported here and these included SOC (sediment oxygen consumption), phosphorus (Dissolved Inorganic Phosphorus or DIP), ammonium, nitrite and nitrite plus nitrate flux. In most case we have only reported nitrite plus nitrate flux because nitrite fluxes were generally very small. During the period when sediment flux measurements were made in Chesapeake Bay and tributary rivers (1978 - 2005) we found 1509 measurements of SOD, 1495 measurements of DIP flux, 1495 measurements of ammonium flux, 1232 measurements of nitrite flux and 1490 measurements of nitrite plus nitrate flux. In a recent review of sediment fluxes for areas other than Chesapeake Bay (Bailey 2005) a total of about 554, 506 and 641 SOC, DIP and ammonium fluxes were identified from 51 other estuaries. The sediment flux measurement density for Chesapeake Bay is much higher than any other estuary that we are aware of and, indeed, the summation of published flux measurements is only about a third the number of measurements made in Chesapeake Bay, tributary rivers and the Maryland Coastal Bays.

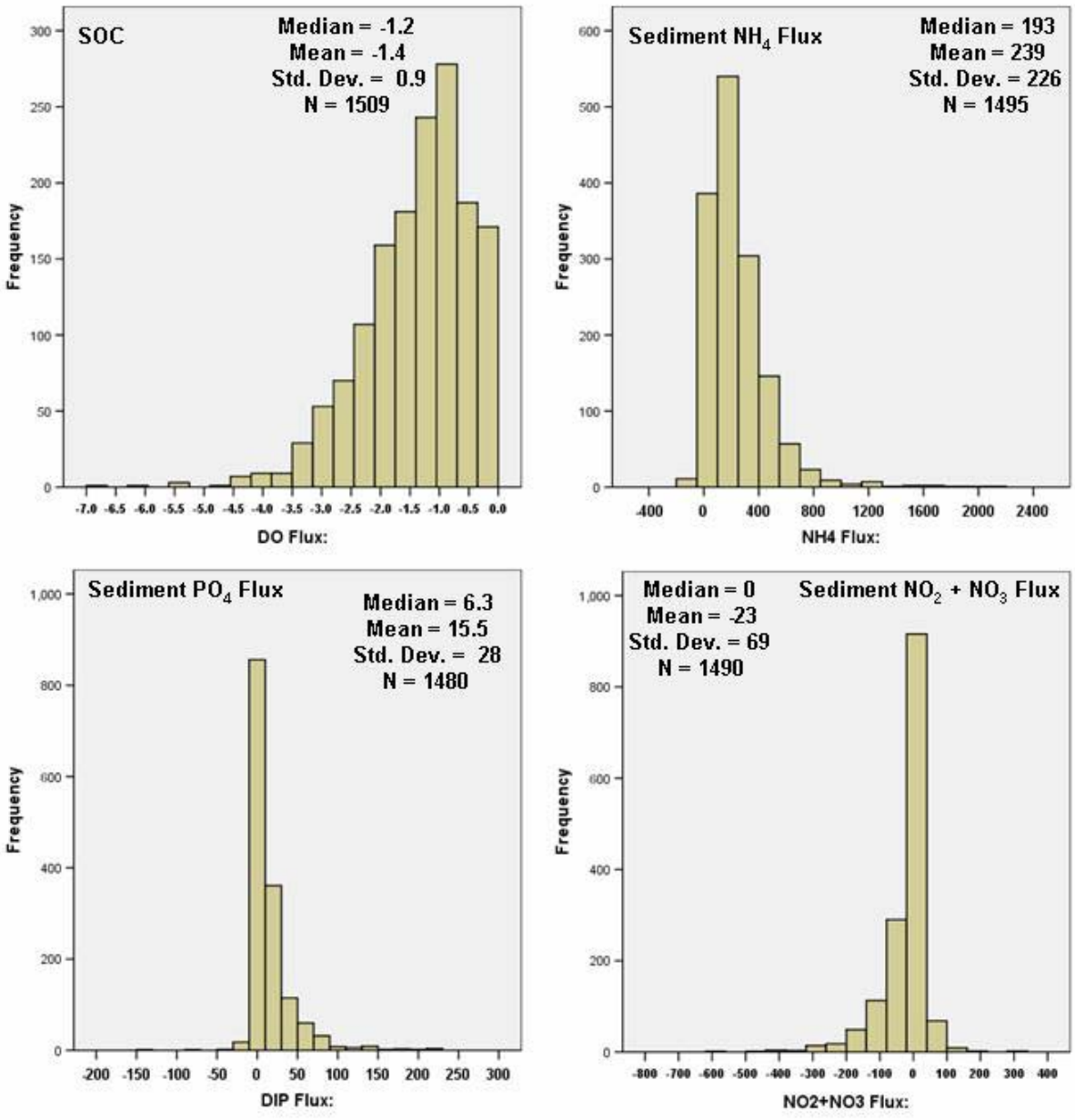

Figure 4-4. *Frequency histograms of sediment water fluxes: SOC (g O_2 m^{-2} d^{-1}), NH_4 (µmoles N m^{-2} h^{-1}), PO_4 (µmoles P m^{-2} h^{-1}) and NO_2+NO_3 (µmoles N m^{-2} h^{-1}) for sediment flux database.*

SOC rates ranged from about zero to 7.0 g O_2 m^{-2} day^{-1} and had a median value of 1.0 g O_2 m^{-2} day^{-1} (Table 4-1; Fig. 4-4). Only about 10% of all SOC measurements exceeded 3 g O_2 m^{-2} day^{-1} but about 24% of measurements were less than 0.75 O_2 m^{-2} day^{-1}. It is important to note that bottom water DO concentration has an effect on SOC rates. We found that at DO concentrations less than about 3 mg $^{-1}$ SOC rates become depressed, apparently due to a lack of DO to support SOC rates. About 24% of all SOC measurements fall into this category. Thus, under normoxic conditions median SOC rate was somewhat higher. It is important to note that sediment metabolism does not cease when bottom water DO concentrations become depressed. Rather, anaerobic metabolism becomes relatively more important. In areas of the Bay where sulfate is available from the water column (e.g., any locations with some salinity) the main form of anaerobic metabolism is sulfate reduction. Unfortunately, there are a limited number of anaerobic metabolism measurements available from Chesapeake Bay. However, measurements made by Roden and Tuttle (1993) and Marvin-DiPasquale et al (1998 and 2003) indicate that anaerobic metabolism is indeed important in Chesapeake Bay sediments, even when DO concentrations in overlying waters are normoxic.

Sediment DIP fluxes ranged from -137 to 229 µmol P m^{-2} hr^{-1} and had a median value of 6.0 µmol P m^{-2} hr^{-1} (Table 4-1; Fig. 4-4). While there were fluxes of DIP from water to sediments, flux in this direction was rare. About 9% of all DIP measurements were sediment-directed. Large sediment-directed fluxes were very rare and almost all sediment-directed DIP fluxes were from tidal freshwater sites. Similarly, very large DIP fluxes were also rare. About 9% of DIP fluxes exceeded 50 µmol P m^{-2} hr^{-1} and were generally associated with very hypoxic or anoxic overlying waters and severely reduced sediments. DIP fluxes exceeded 15 µmol P m^{-2} hr^{-1}in 31% of all bay measurements and these are considered to be of real water quality importance because fluxes of this magnitude could support primary production rates of at least 0.5 g C m^{-2} day^{-1}.

Sediment ammonium fluxes ranged from -148 to 2169 µmol N m^{-2} hr^{-1} and had a median value of 193 µmol N m^{-2} hr^{-1}. A small number of ammonium fluxes were directed from water to sediments (3%) and most of these were quite small (Table 4-1 and Fig. 4-4). The mechanism for sediment ammonium uptake might involve autotrophic utilization or sorption of ammonium to sediments but we have no direct evidence supporting either of these pathways of ammonium loss from the water column. Large ammonium fluxes (>400 µmol N m^{-2} hr^{-1}) were less rare (17% of all measurements) and 30 % of all ammonium fluxes were in excess of 300 µmol N m^{-2} hr^{-1}. Sediment ammonium releases of 300 µmol N m^{-2} hr^{-1} could support phytoplankton production at rates of about 0.7 g C m^{-2} day^{-1}. Highest ammonium fluxes were consistently associated with very nutrient enriched environments of the Bay.

Sediment nitrite plus nitrate fluxes ranged from -607 to 288 µmol N m^{-2} hr^{-1} and had a median value of 0.0 µmol N m^{-2} hr^{-1}. Nitrite plus nitrate flux from water to sediments was the most common flux direction (48% of all fluxes) and it is probable that much of this N was later denitrified in sediments, a conclusion supported by the literature but for which we have no direct evidence from flux monitoring programs. In general nitrite plus nitrate fluxes were correlated with nitrate concentrations in overlying waters. There were a considerable number of nitrite plus nitrate fluxes that were zero (i.e., no net flux) and these comprised 20 % of all fluxes. These mainly occurred during summer at locations removed from river nitrate sources and at locations where bottom water DO

conditions did not permit sediment nitrification. About 32% of all fluxes were from sediments to the overlying water and the magnitude of these fluxes was almost always small (relative to ammonium fluxes) and virtually always small enough to not be a concern from a water quality point of view. However, these nitrite plus nitrate fluxes from sediments to water were a clear indication that nitrification (a process requiring oxygen) was an active process and thus an important indication of well oxygenated sediments and good sediment quality. It is also likely that if sediment nitrification is going on, so is sediment denitrification in sediment layers that are anoxic but very close to the oxidized surficial sediments.

4-5. Sediment Fluxes Compared to Nutrient Loads

In earlier work we developed annual-scale nutrient loading rates to 34 estuarine systems, including a number of sites from Chesapeake Bay and the Maryland Coastal Bays (Boynton et al 2008, in review). N and P loading rates from adjacent watersheds ranged over several orders of magnitude, from 1.1 to 188 g N m^{-2} yr^{-1} and from 0.1 to 32 g P m^{-2} yr^{-1} (Fig. 4-5). Multi-year TN and TP input data for a few estuaries indicate that inter-annual variability can be large, but is not as large as the variability among systems. For example, TN and TP load to the Guadaloupe estuary varied by factors of 3.7 and 2.5, respectively, between wet and dry years. In comparison, TN and TP loading to the Patuxent River estuary varied by 2.0 and 2.6, respectively, during wet and dry years. Kaneohe Bay, HI is an example of significant loading reductions resulting from a diversion of wastewater out of the Bay. TN and TP loads were reduced 2.0 and 4.5-fold respectively, due to management actions related to sewage diversions.

Among the same 34 estuaries, N: P ratios (mass basis) of inputs ranged from 2 to 38, bracketing the Redfield ratio (N: P = 7.2:1 mass ratio). About a quarter of these locations (9 of 34) had load ratios that were considerably lower (<5.0) than the Redfield ratio while 50% (18 of 34) had ratios equal to or higher than 9.0. Although point source dominated systems tend to have lower load ratios (Boynton et al 1995) this is not always the case. For example, several systems (Himmerfjargen,Sweden and Back River, MD) had very high load ratios (38) even though point sources were the dominant nutrient source because P (and not N) was removed from sewage treatment plant effluent.

We can use these inputs shown in Figure 4-5 (often called “new nutrients” because they come from external sources and are introduced into estuaries) as a way of judging the relative importance of nutrients recycled from estuarine sediments. In this figure we have noted average and high values for ammonium and DIP fluxes based on all the data contained in the sediment flux data base. The intersection of the N and P recycling rate lines (for average and high fluxes) describes a box that places Chesapeake Bay sediment fluxes in perspective with “new inputs” of N and P. This plot makes several points quite clear. First, sediment nutrient recycling is important; recycled masses of N and P are equivalent to loading rate in the middle and high range based on a selection of estuaries from around the world. Second, loads of “new nutrients” to systems such as Chesapeake Bay are only part of the eutrophication story. Nutrients are rapidly recycled, from sediments as well as the water column, and used repeatedly, mainly during the warm periods of the year, to maintain and at times enhance eutrophic conditions.

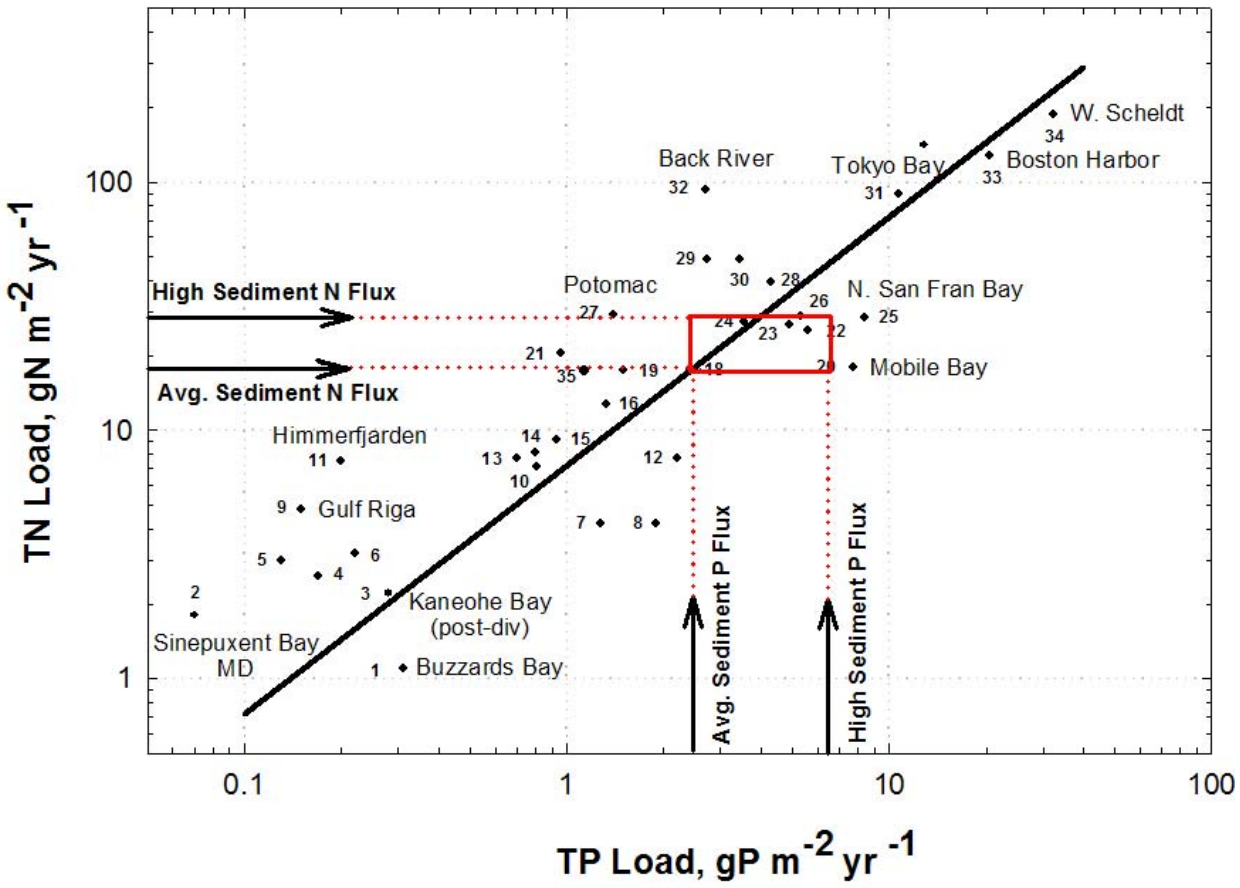

Figure 4-5. *A scatter diagram of total phosphorus (TP) versus total nitrogen (TN) loading rates for a variety of estuarine, coastal and lagoonal ecosystems. The bold horizontal line represents the Redfield ratio (weight basis). The red box indicates the loading rate of N and P delivered as recycled nutrients based on sediment flux data in the Chesapeake Bay sediment flux database. Complete citations for all numbered sites in the diagram can be found in Boynton and Kemp (2008).*

4-6. "Take-Home" Summary

- The flux data set for Chesapeake Bay, tributary rivers and the Maryland Coastal Bays contains measurements from a high diversity of environments. Included are high, moderate and low salinity areas, normoxic, hypoxic and near-anoxic sites and shallow, moderate and deep water sites.
- Approximately 1500 flux measurements are included in the data set and the vast majority of flux measurments also include measurement of selected environmental variables thought to influence (or be influenced by) the pattern and magnitude of sediment fluxes.
- Sediment flux measurements were made in all months of the year but the majority of measurements (72%) were made during the June - August period. Thus, the data set focuses on summer fluxes. However, measurements made during cool and cold periods of the year clearly indicated that sediment fluxes of DO, N and P compounds were small during those periods.
- Descriptive statistics (mean, standard error, median) and frequency histograms have been developed using the entire flux data set for each flux and each environmental variable. Most exhibited substantial ranges of values as expected given the widely differing sediment and water column conditions.
- Compared to "new inputs" of N and P compounds, sediment nutrient releases are large being comparable to loading rates from moderately to very nutrient enriched ecosystems.

4-7. Literature Cited

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Chapter 5

Chesapeake Bay Site-Specific Characterizations

5-1. Introduction

In Chapter 4, Bay-wide patterns of sediment flux and associated environmental variables were examined. In this Chapter sediment fluxes and associated environmental variables are examined at the spatial scale of individual Chesapeake Bay tributaries, the Maryland Coastal Bays and the mainstem Bay. In this section all flux and environmental variables were averaged for summer conditions (June-August) for two reasons: 1) this is the period of the year when sediment processes are most active (see Chapter 6 for details concerning seasonal patterns) and 2) these are the months for which the most sediment flux data are available (72% of the 1509 flux measurements were made in the June-August period). We have included here all tributaries for which there are more than three sediment flux stations. Tributaries are presented from the northern to the southern portion of the Bay system. Each tributary has a set of bar graphs showing flux magnitude along the axis of the estuary and a table summarizing environmental variables at the time flux measurements was made. Stations are listed from up-estuary (left/top) to down-estuary (left/bottom). In a few cases additional graphics have been added to emphasize a particular conclusion.

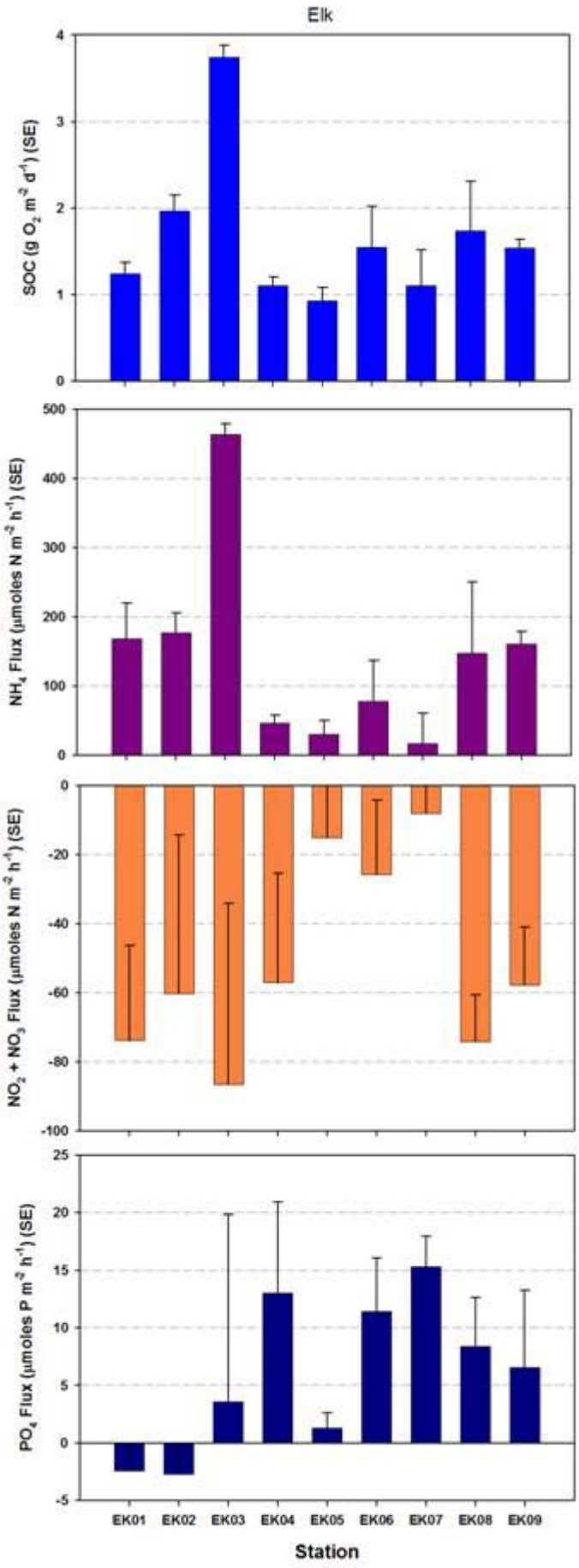
5-1A. Elk River Estuary

Location and General Description

The Elk River estuary is located at the extreme northern portion of Chesapeake Bay (Fig. 3-1 and 5-1; Table 3-3). This small estuary has a surface area of 34 km^2 and an average depth of about 2.4 m. The nominal nitrogen loading rate is 27 g N m^{-2} yr^{-1}. This rate is high compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Elk watershed is primarily natural vegetation (42 %), followed by agricultural uses (33 %). During the period when flux measurements were made (2000) there was no indication of hypoxic bottom waters, although diel scale hypoxia may have been present.

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 1 to 3.6 g O_2 m^{-2} day^{-1} although values at most stations were between 1 and 2 g O_2 m^{-2} day^{-1} (Fig. 5-1). There was one set of very high SOC values recorded in the upper estuary and this was accompanied by a very large ammonium flux. There is nothing in the associated environmental variable data set that suggests a specific reason for this large SOC value. Additional insights concerning sediment biogeochemical processes can be gained by examining the ratio of one sediment flux to another. Perhaps the most useful of these is the SOC to ammonium flux ratio. This ratio (O:N flux ratio; atomic basis) would have a value of about 13 if normal Redfield organic matter (e.g., phytoplankton with C:N:P = 106:16:1) was being aerobically metabolized to end products of carbon dioxide, water and inorganic nutrients. If the ratio departs markedly from 13 we can infer that other processes are occurring in addition to simple aerobic metabolism of phytoplanktonic debris. At all sites in the Elk River the ratio was well above 13, indicating that some remineralized N has been lost.



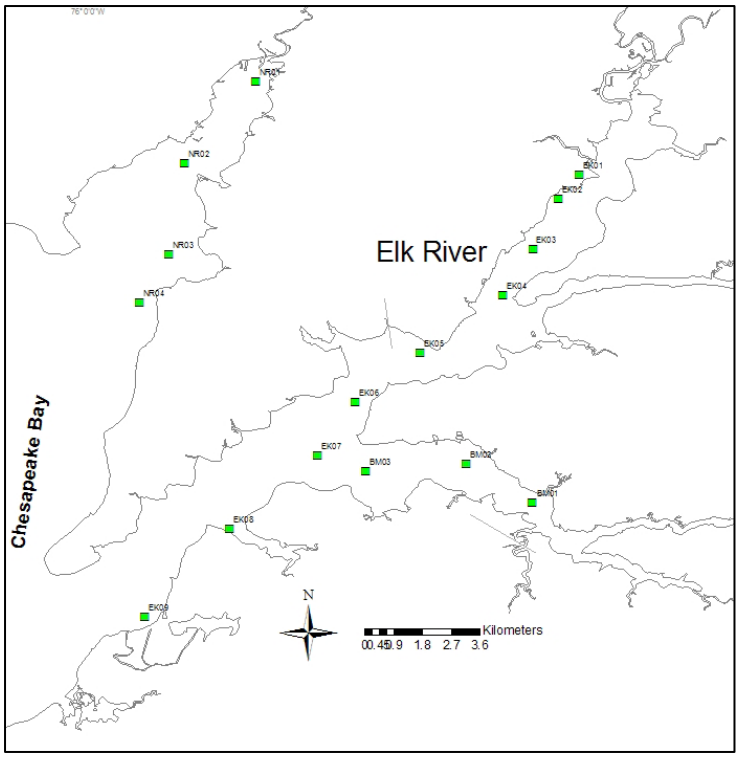


Figure 5-1. *Map of upper Chesapeake Bay showing Elk River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

Ratios of O:N sediment flux at sites in the Elk ranged from about 21 to 75 and were above Redfield proportions at all sites in the estuary. These generally high O:N flux ratios suggest missing nitrogen. N was likely denitrified in sediments, although we do not have direct measurements of denitrification. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 11 days, not a very short turnover time suggesting a reasonably stable DO regime in the water column.

Sediment ammonium fluxes tended to be highest near the head and mouth of the estuary with much smaller values associated with the middle reaches of the estuary (Fig. 5-1). With the exception of this high value (460 µmol N m^{-2} hr^{-1}; Sta. EK03) ammonium fluxes were modest (<200 µmol N m^{-2} hr^{-1}) near the headwaters and near the mouth. Ammonium fluxes in the middle portion of the estuary were very low (< 100 µmol N m^{-2} hr^{-1}). The ammonium fluxes measured in the Elk rank 10th of 13 areas of the Bay and tributaries reported in this section. Sediments in this estuary appear to be well oxidized and there was no indication in this data set of persistent summertime deep water hypoxia. This suggests that coupled nitrification - denitrification may well have been operative, consistent with low sediment ammonium releases. It is also possible that sufficient light reached the bottom in this system and ammonium was being used by sediment autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.6 to 1.2 m (average of 0.8 m) and these indicate that less than 1 % of light reaches the sediment surface at the average depth of the estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this shallow system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Table 5-1. *Summer bottom water conditions for the Elk River estuary.*

Station	$Salinity_b$	DO $(mg\ L^{-1})_b$	$(NO_2 + NO_3)_b$ (µM)	Sed. Chl. *a* $(mg\ m^{-2})_t$	Eh $(mV)_1$
EK01	0.6 ± 0.4	6.9 ± 0.1	45 ± 12	49 ± 4	333 ± 12
EK02	1.2 ± 0.8	6.9 ± 0.3	56 ± 20	63 ± 7	216 ± 31
EK03	1.6 ± 1.1	6.9 ± 0.4	66 ± 24	44 ± 8	176 ± 72
EK04	1.6 ± 1.1	6.9 ± 0.2	81 ± 12	34 ± 5	172 ± 44
EK05	1.8 ± 0.8	6.8 ± 0.3	80 ± 6	61 ± 15	269 ± 63
EK06	1.6 ± 1.0	6.8 ± 0.3	80 ± 9	77 ± 29	298 ± 73
EK07	1.2 ± 0.9	6.8 ± 0.2	73 ± 9	38 ± 8	241 ± 48
EK08	1.0 ± 0.7	7.2 ± 0.2	71 ± 10	54 ± 10	251 ± 61
EK09	0.8 ± 0.7	6.9 ± 0.2	65 ± 12	45 ± 6	156 ± 45

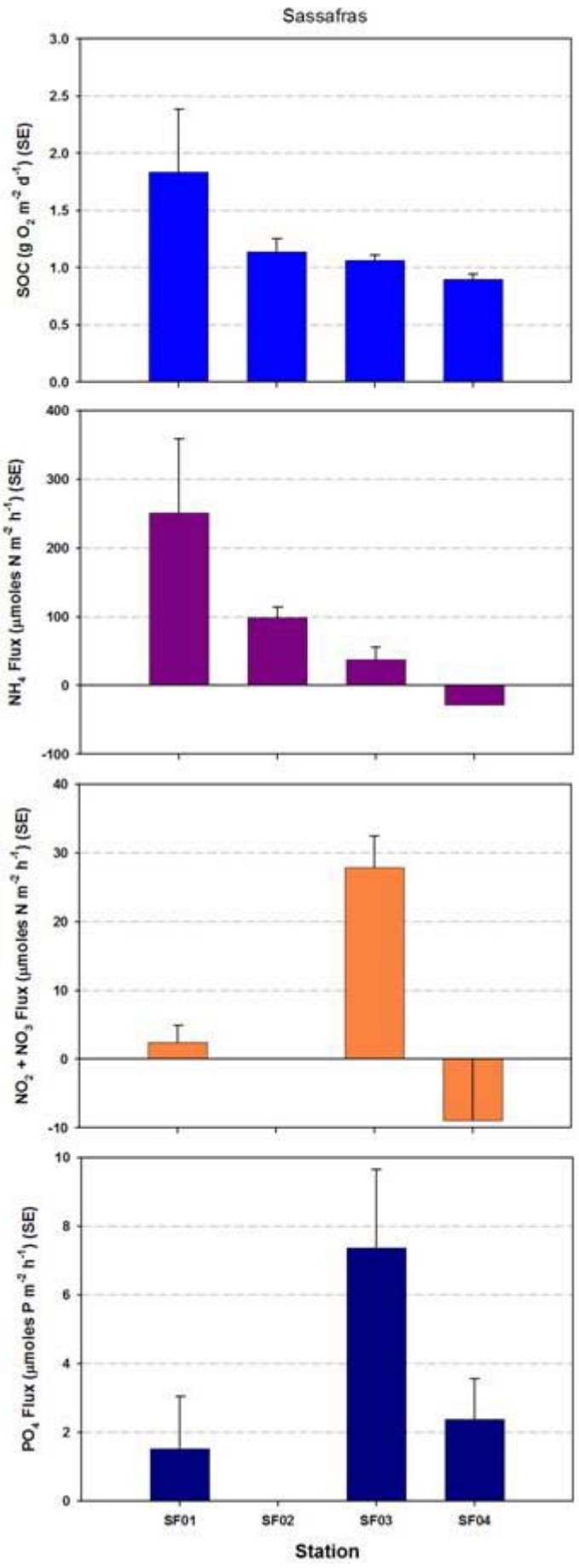
Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were all directed into sediments along the axis of the estuary and the magnitude of flux ranged from quite small in the middle reaches to substantial in the upper and lower estuary (Fig. 5-1). While the flux was from water to sediments, the pattern of NO_2 + NO_3 flux was very similar to that observed for ammonium flux. The fact that these fluxes were directed into sediments was expected given the high levels of NO_3 in the water column (Table 5-1). This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. However, there was a section of the estuary (Sta. EK5-EK7) where fluxes were smaller but the exact reason for this remains unclear. Here again the possibility of autotrophic uptake of nitrate remains but we have no direct evidence to support this possibility. It is also quite possible that sediment nitrification rates at these stations were sufficiently high to reduce the gradient in NO_3 concentrations between the water column and sediments thus reducing the magnitude of NO_3 flux. It would be quite useful to work towards having a denitrification measurement methodology that could be readily incorporated into sediment monitoring programs such as those described here.

Sediment phosphorus flux ranged from about -2 to 15 µmol P m^{-2} hr^{-1}, rates that are generally considered to be small to modest from an impact on water column processes point of view (Fig. 5-1). For example, a sediment P flux of 10 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 0.3 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in most enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at most sites in the Elk River were from sediments to the water column was interesting. At a number of tidal freshwater sites P fluxes tend to be in the opposite direction. There was apparently enough salt in these waters to promote P flux from these iron rich sediments or some other mechanism promoting sediment P-flux was operative (e.g., elevated pH, bioturbation).

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Elk River estuary (Table 5-1). At least during summer conditions this is a turbid, low salinity, very high nitrate and non-hypoxic system. It would be hard to imagine N-limitation of photosynthetic processes, although light limitation is a distinct possibility. Sediment total chlorophyll-a values averaged 52 mg m^{-2}, close to the median value of the full flux data set. These values were about half those routinely observed in more enriched systems. Sediment chlorophyll-a concentration serves as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be a good indicator of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 235 mV, a value indicating oxidized sediments, and an indication, along with high bottom water DO concentrations, that sediment nitrification-denitrification was an active process.



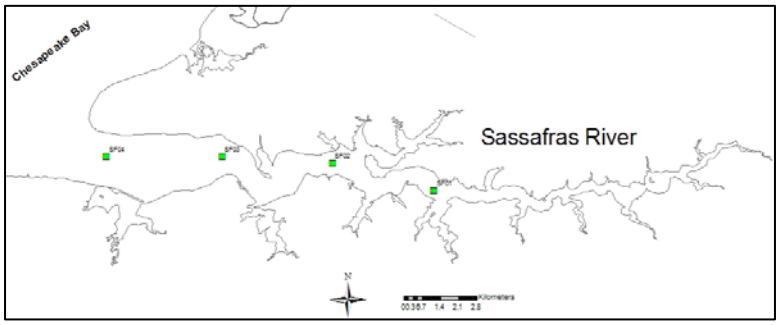


Figure 5-2. *Map of upper Chesapeake Bay showing Sassafras River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

5-1B. Sassafras River Estuary

Location and General Description

The Sassafras River estuary is located at the northern eastern shore portion of Chesapeake Bay (Fig. 3-1 and 5-2; Table 3-3) This small estuary has a surface area of about 36 km^2 and an average depth of about 4.3 m. Nominal nitrogen loading rate is 15 g N m^{-2} yr^{-1}. This rate is moderate compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Sassafras watershed is primarily agricultural (58 %), followed by natural vegetation (26 %). During the period when flux measurements were made (2000) there was no indication of hypoxic bottom waters, although diel scale hypoxia may have been present in shallow water areas.

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 0.9 to 1.7 g O_2 m^{-2} day^{-1} although values at most stations were close to 1 g O_2 m^{-2} day^{-1} (Fig. 5-2), the median rate for the full data set. There was one set of higher SOC values recorded in the upper estuary and this was accompanied by a large ammonium flux. There is nothing in the associated environmental variable data set that suggests a specific reason for this larger SOC value in the upper estuary. However, water residence

time in the upper portions of these estuaries tends to be long, allowing for development and settling of labile plankton material. However, sediment total chlorophyll-a values were not particularly high at this site (Sta. SF01). As described earlier, the ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) would have a value of about 13 if normal Redfield organic matter (e.g., phytoplankton with C:N:P = 106:16:1) was being remineralized. At all sites in the Sassafras River this ratio was well above 13, indicating that some remineralized N was lost and may have been denitrified. Ratios of O:N sediment flux at sites in the Sassafras ranged from about 26 to 92 and were above

Table 5-2. *Summer bottom water conditions for the Sassafras River estuary.*

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
SF01	0.2 ± 0.2	7.2 ± 0.3	8.4 ± 5.7	48 ± 6.8	286 ± 10
SF02	0.2 ± 0.2	6.9 ± 0.2	24 ± 4.6	59 ± 7.7	206 ± 44
SF03	0.2 ± 0.2	7.6 ± 0.2	33 ± 2.9	71 ± 12	77 ± 29
SF04	0.3 ± 0.2	8.0 ± 0.4	49 ± 4.4	42 ± 3.9	250 ± 64

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

Redfield proportions at all sites in the estuary. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 27 days, a very long turnover time suggesting minimal influence of SOC on water column DO conditions.

Sediment ammonium fluxes tended to be highest near the head of the estuary with much smaller values proceeding downstream (Fig. 5-2). With the exception of this higher value (240 µmol N m^{-2} hr^{-1}; Sta. SF01) ammonium fluxes were small (<100 µmol N m^{-2} hr^{-1}) throughout the estuary and ammonium was actually taken up by sediments near the estuary mouth. Ammonium fluxes in the Sassafras ranked 12th of the 13 Bay and tributary sites discussed in this section. Only the Maryland Coastal Bays had lower ammonium fluxes. Sediments in this estuary appear to be well oxidized (average Eh = 205 mV) and there was no indication in this data set of persistent summertime deep water hypoxia. This suggests that coupled denitrification - denitrification may well have been operative, consistent with low sediment ammonium releases. It is also possible that sufficient light reached the bottom in this system and ammonium was being used by sediment autotrophs. In this system there is some support for this suggestion. Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.5 to 1.4 m (average of 1 m) and these suggest that 1 % of light reaches the sediment surface at depths up to almost 3 m and to depths of 4 m in the lower estuary. Some sediment autotrophic activity is possible along the flanks of this shallow system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Sediment nitrite plus nitrate ($NO_2 + NO_3$) fluxes were all small (<30 µmol N m^{-2} hr^{-1}) and directed both into and out of sediments along the axis of the estuary (Fig. 5-2). The fact that these fluxes were not all directed into sediments was expected given the lower concentrations of NO_3 in the water column (Table 5-2). Sediment directed NO_3 flux has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. It is quite possible that sediment nitrification rates at several stations were sufficiently high to reduce the gradient in NO_3 concentrations between the water column and sediments thus reducing the magnitude of sediment NO_3 flux. It is, however, clear that sediment nitrification was taking place at several stations because NO_3 was escaping, at small rates, from sediments to the water column and this, in itself, is an indication of well oxidized sediments.

Sediment phosphorus flux ranged from about 1.5 to 7 µmol P m^{-2} hr^{-1}, rates that are generally considered to be small from an impact on water column processes point of view. For example, a sediment P flux of 7 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 0.2 g C m-2 day-1, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at most sites in the Elk River were from sediments to the water column was interesting. In a number of tidal freshwater sites P fluxes tend to be in the opposite direction. There was apparently enough salt in these waters to promote P flux from these iron rich sediments. The largest sediment P flux observed in the Sassafras was associated with the site having the lowest Eh values recorded for this estuary (SF03; Table 5-2)

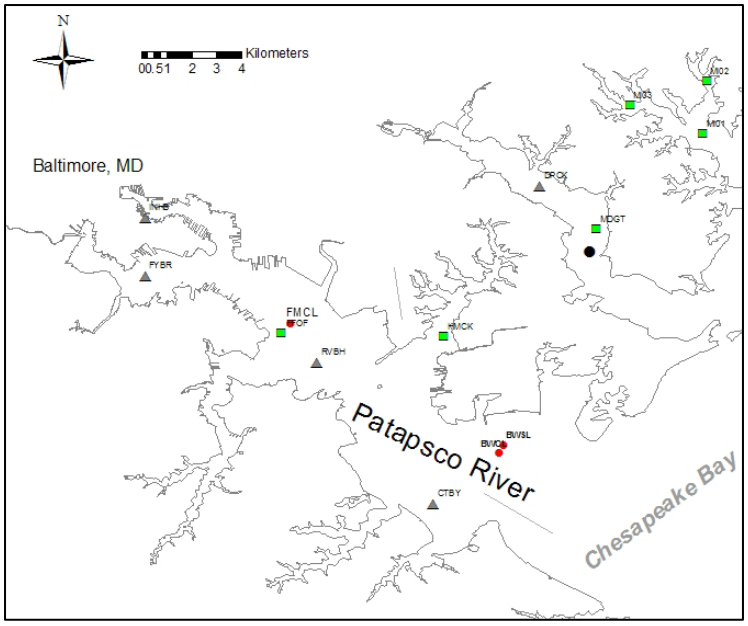
Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Elk River estuary (Table 5-2). At least during summer periods this is a relatively clear, very low salinity, high nitrate and non-hypoxic system. It would be hard to imagine N-limitation of photosynthetic processes, although light limitation is a distinct possibility. It is useful to note that water column nitrate concentrations exhibited an inverse pattern (higher at mouth than near headwaters) and this indicates the strong influence of waters from the Susquehanna River which are high in nitrate, even during summer. Sediment total chlorophyll-a values averaged 55 mg m^{-2}, close to the median value of the full flux data set. These values were about half those routinely observed in more enriched systems. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be good indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 205 mV, a value indicating oxidized sediments, and an indication, along with high bottom water DO concentrations and NO_3 fluxes to the water from sediments, that sediment nitrification-denitrification was an active process.

5-1C. Patapsco River Estuary

Location and General Description

The Patapsco River estuary is located in the northern portion of Chesapeake Bay on the western shore. The City of Baltimore surrounds much of the estuary (Fig. 3-1 and



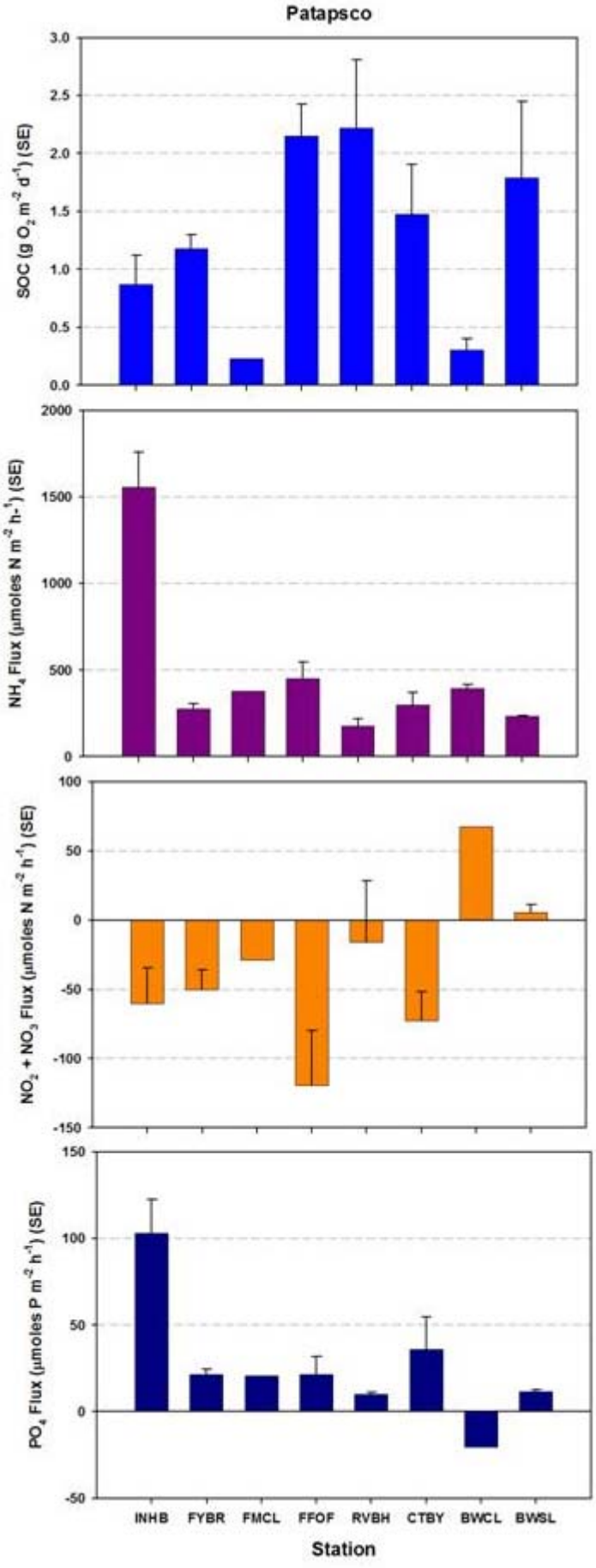


Figure 5-3. *Map of upper Chesapeake Bay showing Patapsco River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

5-3; Table 3-3). This urban estuary has a surface area of about 101 km^2 and an average depth of 4.6 m and much greater depths associated with dredged shipping channels (~12 m). The nominal nitrogen loading rate is 50 g N m^{-2} yr^{-1}. This rate is very high compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Patapsco watershed is almost evenly divided among natural vegetation (30 %), agriculture (34 %) and urban (28%) uses. An estimated 15% of the entire watershed has impervious surfaces. During the period when flux measurements were made (1994-1995, 1997-1998) there were strong indications of persistent hypoxic bottom waters and these conditions can have strong influences on sediment biogeochemistry.

<u>Spatial Pattern and Magnitude of Sediment Flux</u>

SOC rates ranged from about 0.2 to 2.2 g O_2 m^{-2} day^{-1} and tended to be higher

in the mid and mouth areas than in the inner harbor zone (Fig. 5-3). There were several sets of very low SOC values recorded in the estuary (Sta. INHB, FMCL and BWCL) and these were associated with very low bottom water DO concentrations (Table 5-3). In these cases measurements of SOC were limited by DO concentrations. Low SOC measurements at these sites do not indicate low levels of sediment (organic matter) metabolism. In very hypoxic and anoxic sediments anaerobic metabolism is very likely clipping along at very high rates (Roden and Tuttle 1993; Marvin-dePasqualle et al 2003). Dissolved oxygen turnover time based of SOC as the only DO sink (water column

Table 5-3. *Summer bottom water conditions for the Patapsco River estuary.*

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
INHB	8.3 ± 1.3	2.0 ± 0.9	7.2 ± 4.9	49 ± 10	37 ± 57
FYBR	8.0 ± 1.3	4.5 ± 0.9	11.7 ± 3.2	60 ± 6	169 ± 38
FMCL	12.7 ± 1.4	0.2 ± 0.0	7.4 ± 7.2	166 ± 17	76 ± 81
FFOF	6.3 ± 1.7	5.6 ± 0.4	16.7 ± 3.1	164 ± 8	38 ± 25
RVBH	7.2 ± 0.9	4.2 ± 1.5	9.3 ± 2.0	38 ± 10	321 ± 34
CTBY	9.0 ± 1.5	3.2 ± 0.6	11.1 ± 3.1	51 ± 9	272 ± 24
BWCL	13.5 ± 0.8	0.3 ± 0.2	0.2 ± 0.2	157 ± 7	43 ± 40
BWSL	8.8 ± 0.9	3.1 ± 0.4	11.0 ± 5.0	159 ± 2	102 ± 30

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface
ND = No data

DO stock divided by SOC) is about 8 days, a moderately short turnover time. If the stratified summer condition of the Patapsco is considered, the DO turnover time of the deep water is about half that of the full water column or about 4 days. Such short turnover times suggest an important role for sediment processes and a potentially dynamic DO regime. The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) would have a value of about 13 if normal Redfield organic matter (e.g., phytoplankton with C:N:P = 106:16:1) was being remineralized. At most sites in the Patapsco River this ratio was close to or much below the Redfield proportion, indicating that simple remineralization was taking place with little or no coupled sediment nitrification-denitrification. Ratios of O:N sediment flux at sites in the Patapsco River ranged from about 2 to 50 and were above Redfield proportions at only one site in the estuary (Sta. RVBH). It is interesting to note that this site had smaller sediment chlorophyll-a concentration than other sites and by far the most positive Eh values measured in the Patapsco system. At this site we would suggest that coupled nitrification-denitrification was operative and this is a good example of what we might expect for the remainder of the Patapsco if water quality conditions were to vastly improve. While O:N sediment flux ratios in the vicinity of 13 can be explained as remineralization of

phytoplanktonic debris, flux ratios well below 13 require a different explanation. Our interpretation of these is that ammonium is being primarily generated from anaerobic metabolism, mainly based on sulfate reduction. Thus, in oxygen poor zones there is little to no SOC but high rates of anaerobic metabolism generating large amounts of ammonium and hence very low O:N flux ratios.

Sediment ammonium fluxes were extremely high near the head of the Patapsco (in the Inner Harbor area) and were much lower (but still large) throughout the remainder of the estuary (Fig. 5-3). Ammonium fluxes in the Patapsco River ranked 2nd in magnitude of the 13 Bay and tributary sites considered in this section. Ammonium fluxes were larger only in the Anacostia River. Ammonium fluxes at Station INHB were the largest recorded for any site contained in the flux database. With the exception of extreme flux at Station INHB ammonium fluxes were still large (200-400 μmol N m^{-2} hr^{-1}) to the mouth of the estuary. The three highest ammonium fluxes were all associated with low sediment Eh conditions. At many sites in this estuary sediments were quite reduced, associated with persistent summertime deep water hypoxia. This suggests that coupled denitrification - denitrification was not operative, consistent with high sediment ammonium releases. It is unlikely that sufficient light reached the bottom in this system for sediment ammonium to be used by sediment autotrophs. For example, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.6 to 1.3 m (average of 0.9 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the estuary.

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were almost all directed into sediments along the axis of the estuary and the magnitude of flux ranged from quite small (e.g., < 50 μmol N m^{-2} hr^{-1}) at several sites to modest (50 - 100 μmol N m^{-2} hr^{-1}) in other portions of the estuary (Fig. 5-3). The fact that these fluxes were directed into sediments was unexpected given the modest levels of NO_3 in the water column (Table 5-3). This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. The only positive nitrate fluxes were observed near the mouth of the estuary where bottom water quality conditions were generally better than those observed in the inner portions of the estuary

Sediment phosphorus flux ranged from about -22 (at just one site) to about 100 μmole P m^{-2} hr^{-1}, and rates at sites other than INHB (largest rate) and SWCL (negative rate) ranged between 10 and 30 μmol P m^{-2} hr^{-1} (Fig. 5-3). These rates are considered to be modest to large from an impact on water column processes point of view. For example, a sediment P flux of 30 μmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 0.9 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in most enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). Thus, the sediment P fluxes in the Patapsco River estuary can be classified as ranging from large to very large and can be expected to have major impact on water quality conditions, The fact that P flux at most sites in the Patapsco River estuary were from sediments to the water column was interesting and expected. It appears that mechanisms of sediment P release in low salinity waters and sediment P release under hypoxic/anoxic conditions were both operational.

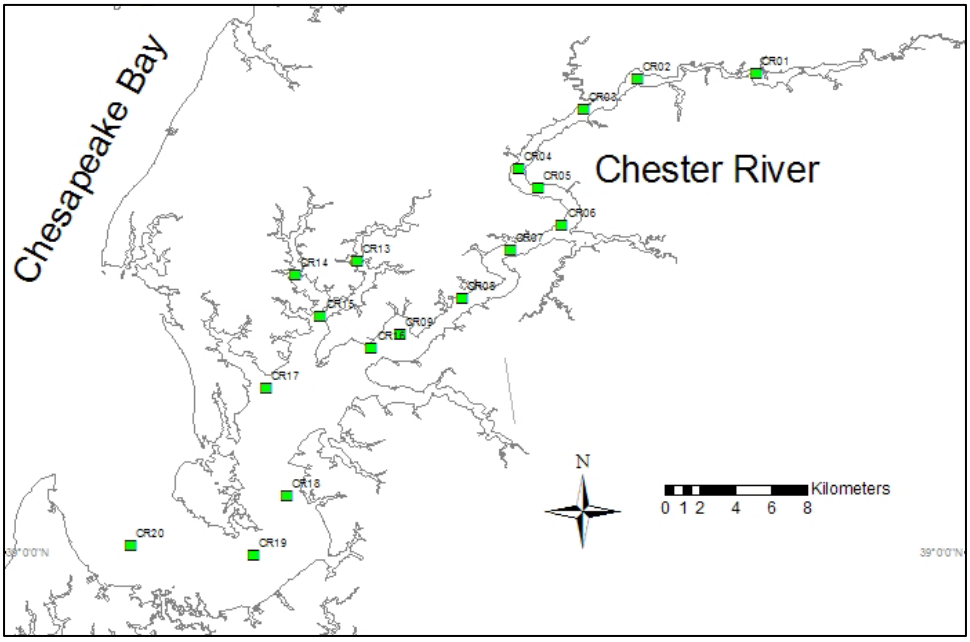
Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Patapsco River estuary (Table 5-3). During summer conditions this is a turbid, low mesohaline (salinity 6-14), low nitrate and chronically hypoxic system. It would be hard to imagine N-limitation of photosynthetic processes, although light limitation is a distinct possibility. Sediment total chlorophyll-a values averaged 106 mg m^{-2}, well above the median value of the full flux data set. These values were similar to those routinely observed in enriched systems, although they were not the highest recorded in the data set (highest values were recorded at enriched sites immediately following the spring bloom deposition in May and June). These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be good indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 106 mV, but were highly variable in this system. There were both relatively high (321 and 272 at Sta. RVBH and CTBY, respectively) and several very low values as well. It is not likely that coupled nitrification-denitrification were active in low Eh sediments during summer periods.

5-1D. Chester River

Location and General Description

The Chester River estuary is located on the eastern shore of Chesapeake Bay and is one of several major eastern shore tributaries (Fig. 3-1 and 5-4; Table 3-3) This estuary is about 62 km in length, has a surface area of about 206 km^2 and an average depth of about 4.1 m. The nominal nitrogen loading rate is 10 g N m^{-2} yr^{-1}. This rate is low compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Chester watershed is primarily agricultural (58 %), followed by natural vegetation 38%), and wetlands (14%). During the period when flux measurements were made (2001) there was no indication of chronic hypoxic bottom waters, although diel scale hypoxia may have been present, especially in shallow areas and in tributary creeks.



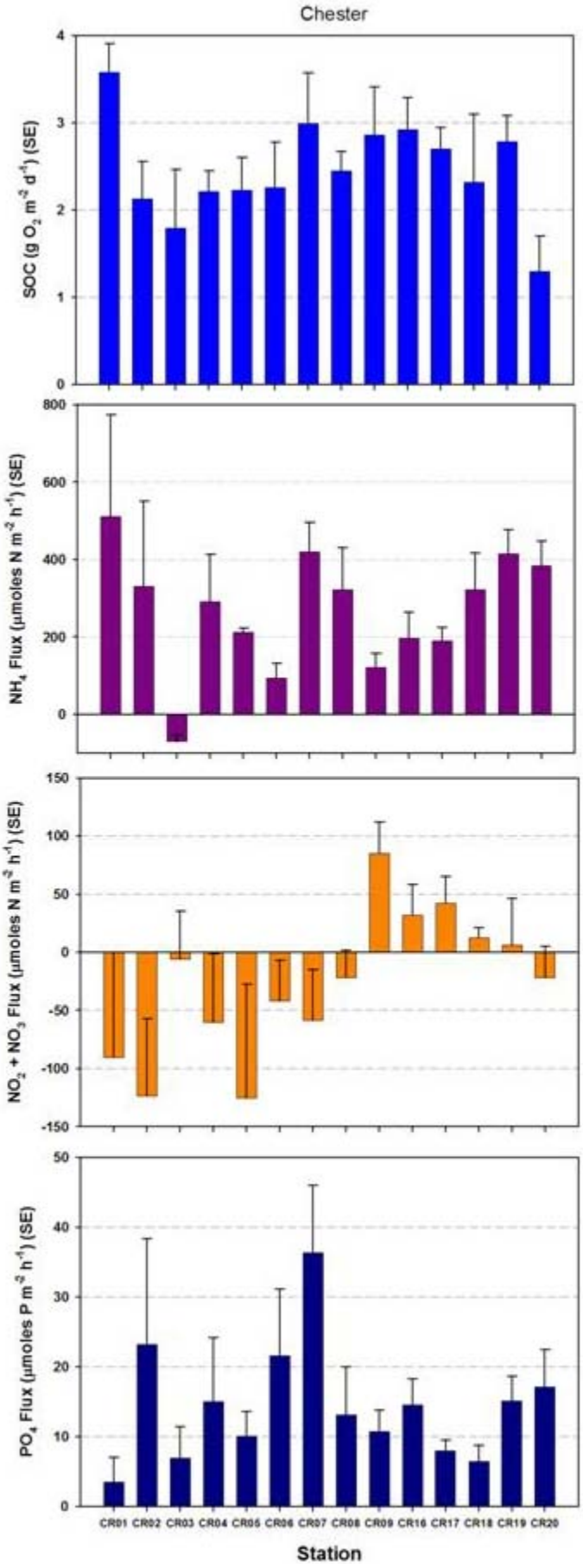


Figure 5-4. *Map of upper Chesapeake Bay showing Chester River sampling sites (on previous page) and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 1.2 to 3.6 g O_2 m^{-2} day^{-1} although values at most stations were between 2 and 3 g O_2 m^{-2} day^{-1} (Fig. 5-4). There was one set of very high SOC values recorded in the upper estuary and this was accompanied by a large ammonium flux. There is nothing in the associated environmental variable data set that suggests a specific reason for this large SOC value. However, the ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (with C:N:P = 106:16:1) is being metabolized. At this site in the Chester the ratio was about 18, a bit above expected for simple remineralization indicating that some remineralized N might have been denitrified or lost through some other process. Ratios of O:N sediment flux at other sites in the Chester ranged from about 10 to 85 and were above Redfield proportions at all but one site (Sta. CR20) at the mouth of the estuary. As indicated earlier, these generally high O:N flux ratios suggest missing nitrogen and that N was likely denitrified in sediments. There was but one relatively low set of SOC values observed at the mouth of the Chester and these low values might have been caused by somewhat depressed bottom water DO values at this site (summer average DO = 2.6 mg l^{-1}). This low DO may reflect importation of low DO water from the mainstem Bay. Dissolved oxygen

turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 13 days, not a very short turnover time, and consistent with the generally high bottom water DO observed in this system.

Table 5-4. *Summer bottom water conditions for the Chester River estuary.*

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
CR01	0.2 ± 0.1	7.5 ± 0.5	61 ± 22	28 ± 16	218 ± 36
CR02	1.1 ± 0.2	5.2 ± 0.3	59 ± 25	88 ± 16	305 ± 37
CR03	2.3 ± 0.2	5.4 ± 0.3	55 ± 21	68 ± 10	372 ± 8
CR04	3.6 ± 0.4	5.3 ± 0.3	48 ± 19	98 ± 24	296 ± 83
CR05	4.3 ± 0.4	5.4 ± 0.4	43 ± 17	52 ± 2	293 ± 19
CR06	5.4 ± 0.5	5.6 ± 0.6	36 ±15	71 ± 15	399 ± 10
CR07	7.8 ± 0.6	5.1 ± 0.8	17 ± 8	80 ± 17	404 ± 11
CR08	9.2 ± 0.5	5.0 ± 0.6	8 ± 4	53 ± 14	407 ± 6
CR09	9.5 ± 0.6	5.6 ± 0.3	7 ± 7	59 ± 12	410 ± 21
CR16	9.7 ± 0.6	5.2 ± 0.3	6 ± 3	74 ± 12	322 ± 25
CR17	10.1 ± 0.7	5.2 ± 1.2	5 ± 4	68 ± 9	387 ± 13
CR18	11.7 ± 0.5	3.7 ± 1.3	3 ± 2	88 ± 12	392 ± 10
CR19	11.7 ± 0.5	4.1 ± 1.0	3 ± 2	101 ± 10	286 ± 76
CR20	12.3 ± 0.6	2.6 ± 1.6	2 ± 2	129 ± 9	171 ± 16

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

Sediment ammonium fluxes tended to be variable along the main axis of the Chester but, with the exception of a few sites, quite high (> 200 µmol N m^{-2} hr^{-1}(Fig. 5-4). Ammonium fluxes in this estuary ranked 5th of the 13 Bay and tributary sites considered in this section. Sediments in this estuary appear to be very well oxidized (mean Eh = 333mV) and there was no indication in this data set of persistent summertime deep water hypoxia, except perhaps at the mouth of the estuary. This suggests that coupled denitrification - denitrification may well have been operative, consistent with lower sediment ammonium releases in several portions of the estuary. It is also possible that sufficient light reached the bottom in this system and ammonium was being used by sediment autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranged from 0.4 to 1.3 m (average of 0.8 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were directed into sediments along the axis of the upper and middle estuary where nitrate concentrations were substantial (Fig. 5-4) and then reversed direction in the lower estuary where water column nitrate concentrations were low. The fact that these up-estuary fluxes were directed into sediments was expected given the high levels of NO_3 in the water column (Table 5-4). This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. However, in the lower portion of the estuary nitrate was being released by sediments and this is a sign of surficial sediment nitrification, an index we use to indicate good sediment quality. The generally high sediment Eh values further support this contention. It is also interesting to note that at three sites in the mid to lower estuary (Sta. CR09, CR16 and CR 17) ammonium fluxes were depressed relative to those measured immediately up and down estuary. At these sites nitrate fluxes from sediments to the water column were the largest measured in this estuary suggesting that some of the ammonium remineralized in sediments was nitrified rather than released as ammonium. We would suggest that much of the nitrified N is denitrified but we have no direct measurements of this process. It would be quite useful to work towards having a denitrification measurement methodology that could be readily incorporated into sediment monitoring programs such as those described here.

Sediment phosphorus flux ranged from about 4 to 35 µmol P m^{-2} hr^{-1}, rates that are generally considered to be modest to large from an impact on water column processes point of view. Sediment P fluxes averaged about 15 µmol P m^{-2} hr^{-1} in the Chester. A sediment P flux of 15 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 0.5 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at most sites in the Chester River were from sediments to the water column was interesting; there was apparently enough salt in these waters to promote P flux from these sediments despite of there being no indication of severe hypoxia.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Chester River estuary (Table 5-4). At least during summer conditions this is a turbid, low salinity, high nitrate and non-hypoxic system. It would be hard to imagine N-limitation of photosynthetic processes, although light limitation is a distinct possibility. Sediment total chlorophyll-a values averaged 76 mg m^{-2}, slightly higher than the median value of the full flux data set. These values were about half those routinely observed in more enriched systems. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be a good indicator of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 333 mV, a value indicating oxidized sediments, and an indication, along with high bottom water DO concentrations, that sediment nitrification-denitrification was an active process.

5-1E. Corsica River

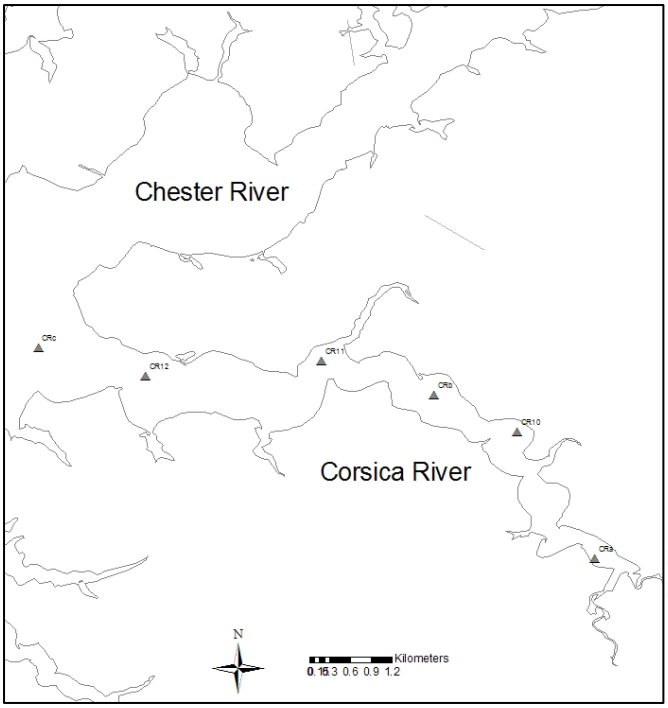
Location and General Description

The Corsica River estuary is located on the eastern shore of Chesapeake Bay and is a tributary of the much larger Chester River estuary (Fig. 3-1 and 5-5; Table 3-3) This estuary is about 8 km in length, has a surface area of about 5.4 km^2 and an average depth of about 1.9 m. The nominal nitrogen loading rate is 22 g N m^{-2} yr^{-1}, respectively. This rates is comparable compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Corsica watershed is primarily agricultural (64 %), followed by natural vegetation (28%). A modest portion is wetlands (9 %). During the period when flux measurements were made (2001 and 2006) there was no indication of chronic hypoxic bottom waters, although diel scale hypoxia was certainly present and severe, as indicated by Bay Program ConMon meters placed in several regions of this small estuary. (www.eyesonthebay.net).

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 1.8 to 3.3 g O_2 m^{-2} day^{-1} although values at most stations were between 2 and 3 g O_2 m^{-2} day^{-1} (Fig. 5-5). There was one set of lower SOC values recorded in the upper estuary (Sta. CR10) and this was associated with the lowest average bottom water DO concentrations. In this case, water column DO may have been limiting SOC rates. The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (with C:N:P = 106:16:1) is being metabolized. At all but one site in the Corsica the ratio was close to or slightly below Redfield proportions, indicating that little of the remineralized N was denitrified or that there were other sediment sources of ammonium (i.e., from anaerobic metabolism). Ratios of O:N sediment flux at the most up estuary site (Sta. CRA) were very high consistent with significant N loss given rates of oxygen use by sediments. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 3.3 days, a very short turnover time, and consistent with the very large diel oscillations observed with the ConMon Program. Dissolved oxygen conditions in this estuary are very dynamic and unstable.

Sediment ammonium fluxes tended to be very high along the main axis of the Chester (> 400 µmol N m^{-2} hr^{-1}) with the exception of one site at the head of the estuary where ammonium releases were much lower (Fig. 5-5). Ammonium fluxes in this estuary ranked 3th of the 13 Bay and tributary sites considered in this section. Sediments in this estuary appear to be generally oxidized (mean Eh = 178mV) but there were sites where Eh values were low (< 55 mV; Sta. CRA and CRB). While there was no indication in this data set of persistent summertime bottom water hypoxia, except perhaps at Station CR10, there is ample evidence of severe diel-scale hypoxia based on ConMon data. This suggests that coupled denitrification - denitrification may well have been compromised during low DO periods of the day. It is also possible that some light reached the bottom in this system and ammonium was being used by sediment autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.3 to 0.75 m (average of 0.5 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the



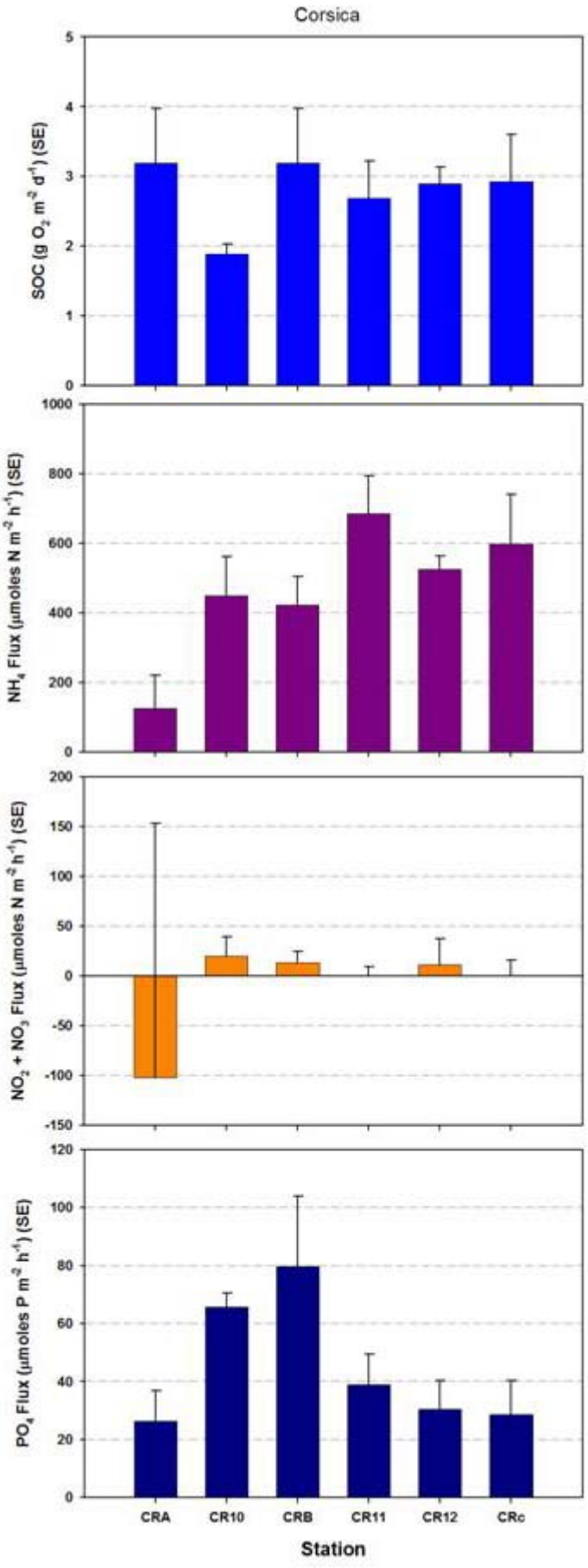


Figure 5-5. *Map of upper Chesapeake Bay showing Corsica River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this system and towards the mouth of the estuary and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005). However, ammonium fluxes were indeed high in this small system.

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were directed into sediments at the head of the estuary where nitrate concentrations were slightly elevated (8.1 uM; Table 5-5) and then reversed direction in the remainder of the estuary where water column nitrate concentrations were low. The fact that these up-estuary fluxes were directed out of sediments was expected given the relatively low levels of NO_3 in the water column (Table 5-5). However, in the other portions of the estuary nitrate was being released by sediments (at very low rates) and this is a sign of surficial sediment

nitrification, an index we use to indicate good sediment quality. The generally high sediment Eh values further support this contention. Given that very low bottom water DO concentrations have been recorded at ConMon stations in the Corsica (diel-scale hypoxia) we were somewhat surprised to see evidence of sediment nitrification at most stations. We would suggest that much of the nitrified N is denitrified but we have no direct measurements of this process. It would be quite useful to work towards having a denitrification measurement methodology that could be readily incorporated into sediment monitoring programs such as those described here.

Sediment phosphorus flux ranged from about 25 to 80 µmol P m^{-2} hr^{-1}, rates that are generally considered to be very large from an impact on water column processes point of view. Sediment P fluxes averaged about 40 µmol P m^{-2} hr^{-1} in the Corsica during the summer period. A sediment P flux of 40 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 1.2 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at all sites in the Corsica River were from sediments to the water column was interesting; there was apparently enough salt in these waters to promote P flux from these sediments despite there being no indication of continuously severe hypoxia.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Corsica River estuary (Table 5-5). At least during summer conditions this is a turbid, low to mid salinity, low nitrate and diel-scale hypoxic system. It would be hard to imagine N-limitation of photosynthetic processes, although light limitation is a distinct possibility. Sediment total chlorophyll-a values averaged 102 mg m^{-2}, higher than the median value of the full flux data set. These values were more

Table 5-5. *Summer bottom water conditions for the Corsica River estuary.*

Station	$Salinity_b$	DO $(mg\ L^{-1})_b$	$(NO_2 + NO_3)_b$ (µM)	Sed. Chl. *a* $(mg\ m^{-2})_t$	Eh $(mV)_1$
CRA	6.0 ± 1.0	8.1 ± 0.5	0.8 ± 0.3	84 ± 15	53 ± 89
CR10	8.9 ± 0.8	2.5 ± 1.1	0.6 ± 0.3	121 ± 14	259 ± 20
CRB	7.7 ± 1.1	5.1 ± 1.0	0.7 ± 0.4	81 ± 11	37 ± 86
CR11	9.2 ± 0.7	3.7 ± 1.1	1.3 ± 1.0	104 ± 4	227 ± 60
CR12	10.1 ± 0.7	4.2 ± 0.6	3.5 ± 2.7	99 ± 7	387 ± 9
CRC	8.6 ± 1.1	6.1 ± 0	2.7 ± 1.0	120 ± 7	105 ± 130

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

than half those routinely observed in very enriched systems. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be good indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 105 mV, a value indicating marginally oxidized sediments, and an indication, along with modest bottom water DO concentrations, that sediment nitrification-denitrification was an active process, but possibly somewhat compromised by poor diel DO conditions.

5-1 F. Severn River

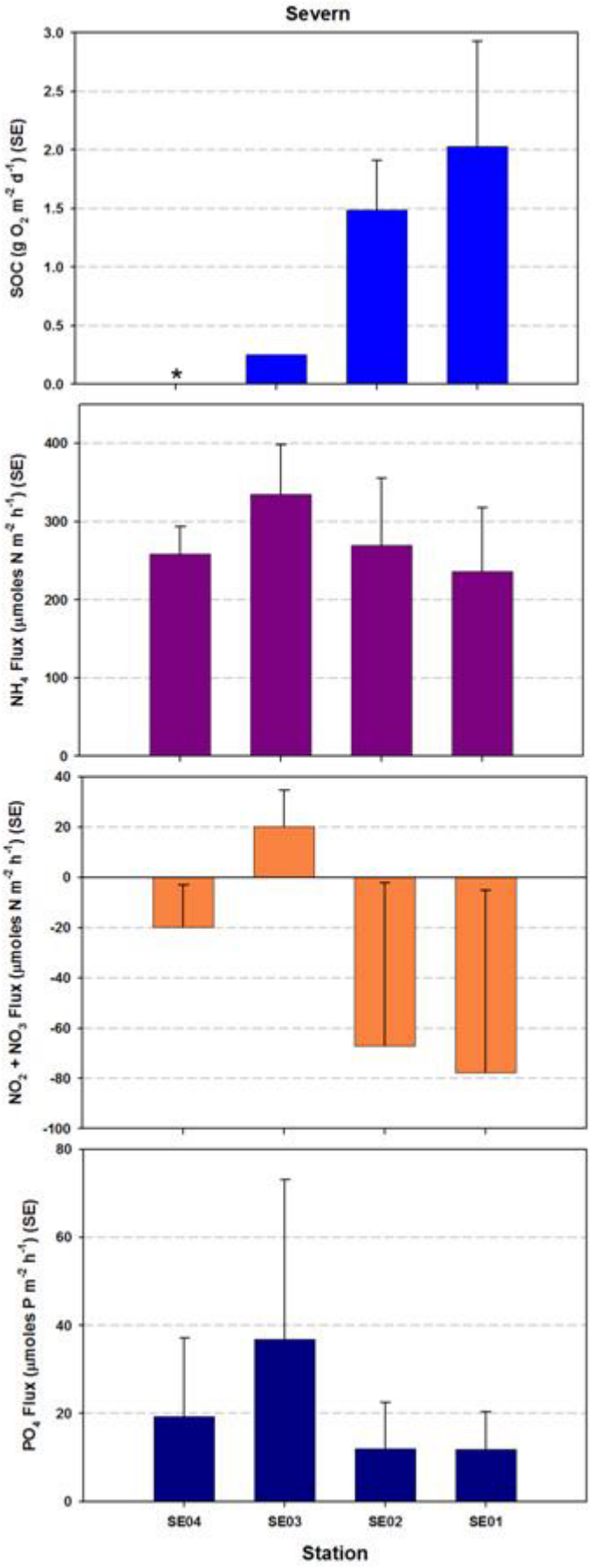
Location and General Description

The Severn River estuary is located on the western shore of Chesapeake Bay at Annapolis, MD (Fig. 3-2 and 5-6; Table 3-1) This estuary is about 18 km in length, has a surface area of about 40 km^2 and an average depth of about 3.8 m. Land use in the Severn watershed is primarily natural vegetation (46 %), followed by developed (28%) and cultivated (15%) land; there is very little wetland associated with the Severn (3 %). However, just over 9% of the basin has impervious surfaces. During the period when flux measurements were made (2005) there were strong indications of chronic hypoxic bottom waters; diel scale hypoxia was also present, as indicated by Bay Program ConMon meters placed in this estuary. (www.eyesonthebay.net).

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 0 to 2.0 g O_2 m^{-2} day^{-1} (Fig. 5-6). There were two sets of SOC measurement near zero and these occurred because water column DO concentrations were effectively zero at these sites (Sta. SE04 and SE03). In these cases, water column DO was limiting SOC rates although anaerobic respiration rates were probably quite large. The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (phytoplanktonic debris with C:N:P = 106:16:1) is being metabolized. At two upriver sites in the Severn the ratio was much below Redfield proportions (<1), indicating that no N was lost to denitrification and that a good deal of ammonium was being generated from anaerobic metabolism. Ratios of O:N sediment flux at the two down estuary sites (SE02 and SE01)) were high, consistent with significant N loss given rates of oxygen use by sediments. It is instructive to know that bottom water DO and sediment Eh conditions at these sites were more conducive to nitrification and linkage to denitrification. The data collected in the Severn also indicate the definitive differences (over small spatial scales of a few kilometers) that can occur in sediment biogeochemistry in relation to sediment and water quality conditions. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 7 days, a short turnover time, and consistent with the large diel oscillations observed with the ConMon Program. Dissolved oxygen conditions in this estuary are very dynamic, unstable and very low in the upper estuary.

Sediment ammonium fluxes tended to be high along the main axis of the Severn (> 200 µmol N m^{-2} hr^{-1}; Fig. 5-6). Ammonium fluxes in this estuary ranked 7th of the 13 Bay and tributary sites considered in this section. Ammonium fluxes ranged from about 220 to 330 µmol N m^{-2} hr^{-1}. Sediments in this estuary exhibited a very strong and consistent gradient in Eh values ranging from -21 in the upper estuary to 227 at the



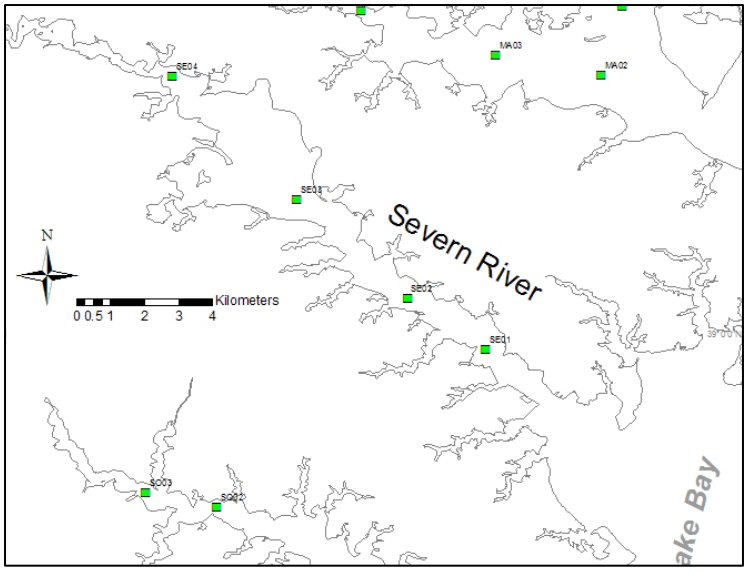


Figure 5-6. *Map of upper Chesapeake Bay showing Severn River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

estuary mouth. This strong gradient (similar gradient in bottom water DO concentrations) suggests that coupled denitrification - denitrification may well have been compromised in the upper but not lower estuary, as indicated by O:N sediment flux ratios. Sediment ammonium flux can also be restricted if light reached the bottom to support growth of sediment autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranged from 0.7 to 0.9 m (average of 0.8 m) and these suggest that much less than 1 % of light reached the sediment surface at the average depth of the estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005). However, ammonium fluxes were substantial in this small system and probably played an important role in creating the poor water quality conditions observed during 2005.

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were directed both into sediments at the mouth of the estuary where nitrate concentrations were slightly elevated (5 to 7

µM; Fig. 5-6; Table 5-6) and then were very small in the remainder of the estuary where water column nitrate concentrations were low and sediment quality poor (i.e., low DO and very low Eh values). Nitrate plus nitrite fluxes ranged from 20 to -78 µmol N m^{-2} hr^{-1}. The fact that these down estuary fluxes were directed into sediments was expected given modest levels of NO3 in the water column (Table 5-6).

Sediment phosphorus flux ranged from about 10 to 36 µmol P m^{-2} hr^{-1}, rates that are generally considered to be modest from an impact on water column processes point of view. Sediment P fluxes averaged about 18 µmol P m^{-2} hr^{-1} in the Severn during the summer period. For example, a sediment P flux of 18 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 0.6 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates

Table 5-6. Summer bottom water conditions for the Severn River estuary.

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
SE04	9.1 ± 0.7	0.2 ± 0.3	0.4 ± 0.2	138 ± 20	-21 ± 107
SE03	9.6 ± 0.8	0.1 ± 0.3	0.6 ± 0.3	93 ± 16	78 ± 69
SE02	9.9 ± 0.8	2.9 ± 0.8	5.4 ± 4.1	79 ± 19	163 ± 79
SE01	9.9 ± 0.6	4.9 ± 0.8	7.3 ± 6.2	84 ± 23	227 ± 81

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at all sites in the Severn River were from sediments to the water column was interesting; there was apparently enough salt at the more normoxic sites and hypoxia/anoxia at the upper estuary sites to promote P flux throughout the estuary.

Environmental Conditions

During summer conditions the Severn River estuary is a turbid, low to mid salinity, low nitrate and hypoxic system (Table 5-6). It would be hard to imagine N-limitation of photosynthetic processes in this estuary, although light limitation is a distinct possibility. Sediment total chlorophyll-a values averaged 112 mg m^{-2}, higher than the median value of the full flux data set. These values were more than half those routinely observed in very enriched systems. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be good indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values exhibited a very strong gradient down the axis of the estuary being quite reduced up estuary and oxidized towards the mouth. Bottom water DO concentrations followed a similar pattern. Thus, it is likely that if sediments were losing N via denitrification this process would be more important at the mouth than the headwaters. Finally, this is one of several tributaries of the upper Bay that exhibit inverse

patterns. Specifically, there is almost no salinity gradient and nitrate plus nitrite concentrations increase in a down estuary direction. This is the opposite seen in larger tributaries. This effect is likely caused by the very substantial influence the Susquehanna River has on these small systems in the upper portion of the Bay.

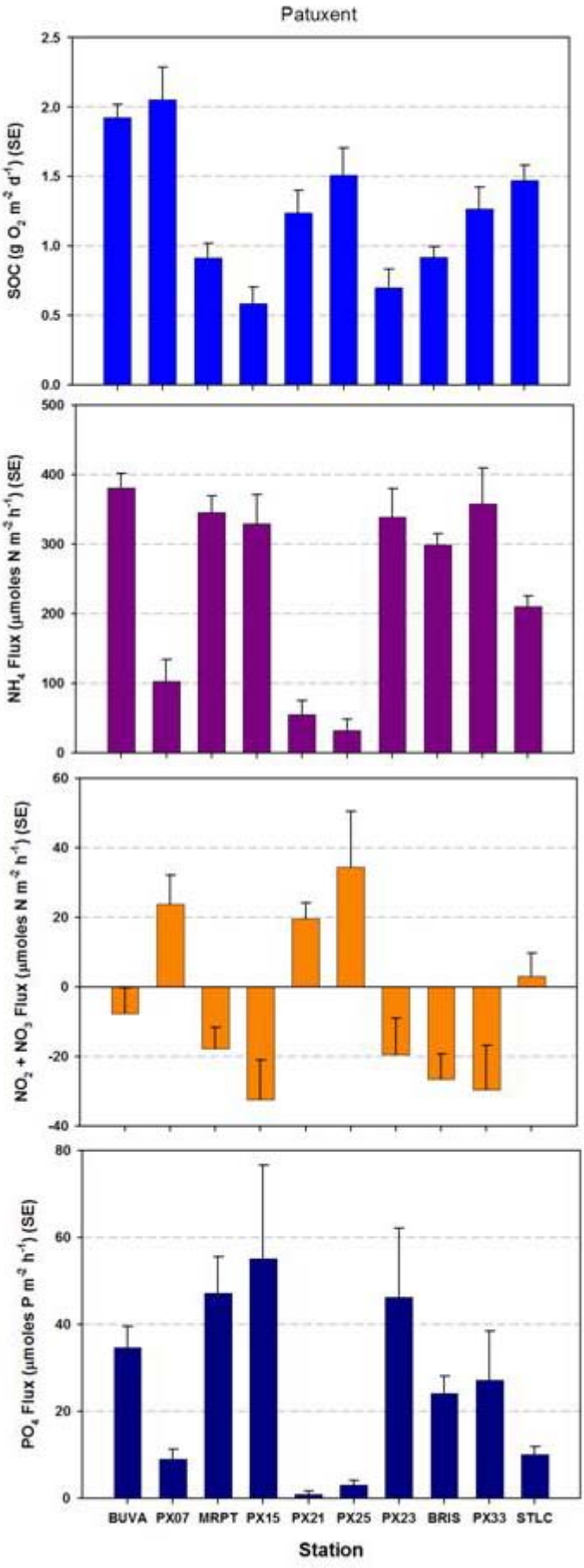
5-1G. Patuxent River

Location and General Description

The Patuxent River estuary is located on the western shore of Chesapeake Bay and is one of several major western shore tributaries (Fig. 3-1 and 5-7; Table 3-3) This estuary is about 92 km in length, has a surface area of 143 km^2 and an average depth of about 6 m. The nominal nitrogen loading rate is 20 N m^{-2} yr^{-1}. This rate is similar to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Patuxent watershed is primarily natural vegetation (40 %), followed by agriculture (34%), and developed land. During the period when flux measurements were made (many years; 1977-1996) there were clear indications of chronic hypoxic bottom waters in the mesohaline portion of the estuary, and diel scale hypoxia was present in shallow areas and in tributary creeks. Information on sediment flux in this estuary has been published by Boynton et al (1980), Boynton and Kemp (1985) and Boynton et al (2008). Sediment flux measurements in this estuary are very numerous but are all from the mesohaline region of the estuary.

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 0.6 to 2.1 g O_2 m^{-2} day^{-1} although values at most stations were between 1 and 2 g O_2 m^{-2} day^{-1} (Fig. 5-7). SOC rates in the Patuxent ranked 8th of the 13 estuaries considered in this section. There were several sets of low SOC values recorded in the estuary (e.g., Sta. MRPT, PX15, PX23 and PX33) and all of these were associated with low (<3 mg l^{-1}) bottom water DO concentrations (Table 5-7). In these cases measurements of SOC were limited by DO concentrations. Low SOC measurements at these sites do not indicate low levels of sediment (organic matter) metabolism. In hypoxic and anoxic sediments anaerobic metabolism is very likely clipping along at very high rates (Roden and Tuttle 1993; Marvin-dePasqualle et al 1998, 2003). The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (phytoplankton organic matter with C:N:P = 106:16:1) is being metabolized. At sites in the Patuxent this ratio varied a great deal, ranging from 6 to about 180. However, all sites exhibiting high O:N flux ratios were from shallow sites. Flux ratios at or below Redfield proportions were from sites deeper than 5 m. As indicated earlier, generally high O:N flux ratios suggest missing nitrogen and that N was likely denitrified in sediments (Boynton and Kemp 1985). This pattern suggests that in those sites (shallow sites, for example) where sediments remain well oxidized because of a short and well-mixed water column, coupled nitrification-denitrification is active through the summer months. In contrast, at deeper sites that experience hypoxia during summer O:N flux ratios indicate simple remineralization of N to ammonium with no loss to denitrification. In cases where the O:N flux ratio is well below the expected 13, we suggest some additional N may have come from sulfate-based anaerobic respiration. The important management point here is that if DO in bottom waters can be elevated (>3 mg l^{-1}) a good deal of N that is now recycled many times



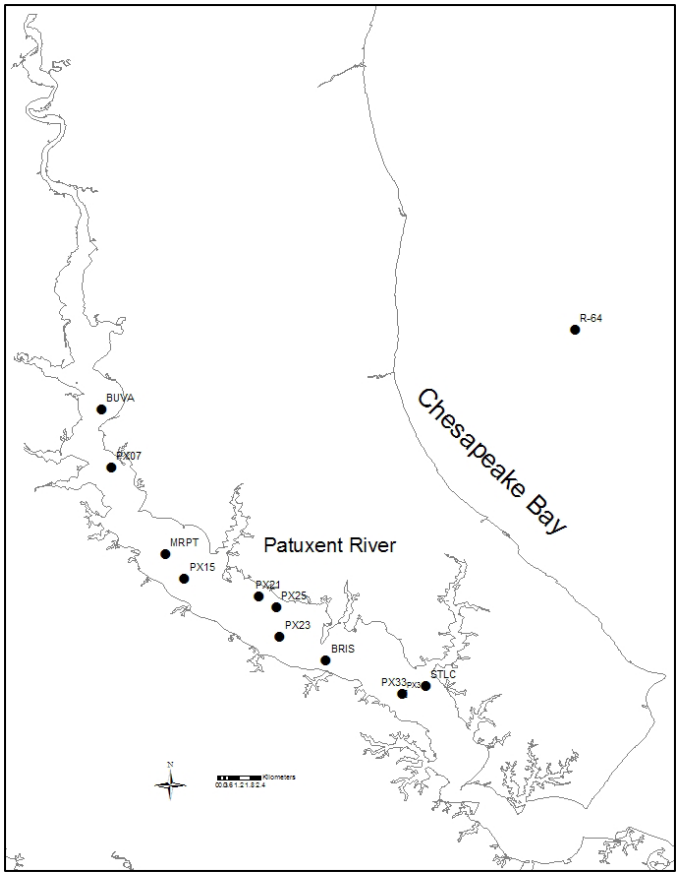


Figure 5-7. *Map of upper Chesapeake Bay showing Patuxent River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

during the warm months and supports additional phytoplankton blooms, would be effectively removed from the system. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 16 days, not a very short turnover time. However, if we consider just the portion of the water column beneath the seasonal pycnocline, the turnover time is reduced by about a factor of two.

Sediment ammonium fluxes were variable along the main axis of the Patuxent but, with the exception of several sites, quite high (> 300 µmol N m^{-2} hr^{-1}(Fig. 5-7)). Ammonium fluxes in this estuary ranked 6th of the 13 Bay and tributary sites

considered in this section. Sediments in this estuary had a mean Eh = 209mV but were also quite variable. At those stations with reduced ammonium fluxes, Eh values were elevated indicating persistently oxidized sediments. This suggests that coupled denitrification - denitrification may well have been operative, consistent with lower sediment ammonium releases at these sites in the estuary. Jenkins and Kemp (1984) reported a lack of sediment denitrification in deeper waters of the Patuxent during summer, probably because of a lack of dissolved oxygen needed to support nitrification. It is also possible that sufficient light reached the bottom in this system and ammonium was being used by sediment autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.6 to 1.3 m (average of 0.9 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were directed both into and out of sediments along the axis of the estuary (Fig. 5-7). Nitrate plus nitrite fluxes ranged from -33 to 35 μmol N m^{-2} hr^{-1}. Fluxes into sediments were likely in response nitrate in the water column although nitrate concentrations were not high in this system, in part because these are summer measurements and in part because all the sites were located in the mesohaline estuary where nitrate concentrations are typically low (Table 5-7). This pattern of nitrate flux has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. However, at the shallow sites of the estuary nitrate was being released by sediments and this is a sign of surficial sediment nitrification, an index we use to indicate good sediment quality. The generally high sediment Eh values further support this contention. It is also interesting to note that at these four sites (Sta. PX07, PX21, PX25 and STLC), ammonium fluxes were depressed relative to those measured in adjacent but deeper water. At these sites nitrate fluxes from sediments to the water column were substantial suggesting that some of the ammonium remineralized in sediments was nitrified rather than released as ammonium. We would suggest that much of the nitrified N is denitrified but we have no direct measurements of this process. It would be quite useful to work towards having a denitrification measurement methodology that could be readily incorporated into sediment monitoring programs such as those described here.

Sediment phosphorus flux ranged from about 1 to 55 μmol P m^{-2} hr^{-1}, rates that are generally considered to be modest to large from an impact on water column processes point of view. Sediment P fluxes averaged about 25 μmol P m^{-2} hr^{-1} in the Patuxent. A sediment P flux of this magnitude could support a phytoplanktonic production rate of about 0.8 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at all sites in the Patuxent River were from sediments to the water column was interesting; there was apparently enough hypoxia in these waters to promote P flux from these sediments except in the very shallow sites where very oxidized and iron-rich sediments likely trapped phosphorus before it could be released to the overlying water.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Patuxent River estuary (Table 5-7). At least during summer conditions this is a turbid, mid-salinity, low nitrate and hypoxic system. Nitrogen limitation of photosynthetic processes has been repeatedly demonstrated

Table 5-7. Summer bottom water conditions for the Patuxent River estuary.

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
BUVA	9.9 ± 0.4	4.5 ± 0.2	3.6 ± 0.8	70 ± 6	265 ± 17
PX07	9.9 ± 0.9	4.9 ± 0.5	2.1 ± 0.6	63 ± 9	337 ± 21
MRPT	12.2 ± 0.4	2.1 ± 0.3	3.1 ± 0.7	78 ± 7	170 ± 22
PX15	12.2 ± 0.4	1.0 ± 0.3	3.2 ± 1.1	131 ± 14	103 ± 33
PX21	10.3 ± 1.0	6.2 ± 0.4	0.8 ± 0.3	36 ± 3	271 ± 33
PX25	11.0 ± 1.0	6.0 ± 0.4	0.8 ± 0.3	42 ± 6	253 ± 38
PX23	12.4 ± 0.9	1.2 ± 0.3	3.4 ± 1.2	117 ± 12	129 ± 34
BRIS	13.1 ± 0.5	2.1 ± 0.2	4.1 ± 0.6	86 ± 6	158 ± 20
PX33	12.1 ± 1.1	2.0 ± 0.4	4.1 ± 1.3	125 ± 11	187 ± 48
STLC	12.8 ± 0.4	3.9 ± 0.2	3.2 ± 0.5	88 ± 6	216 ± 22

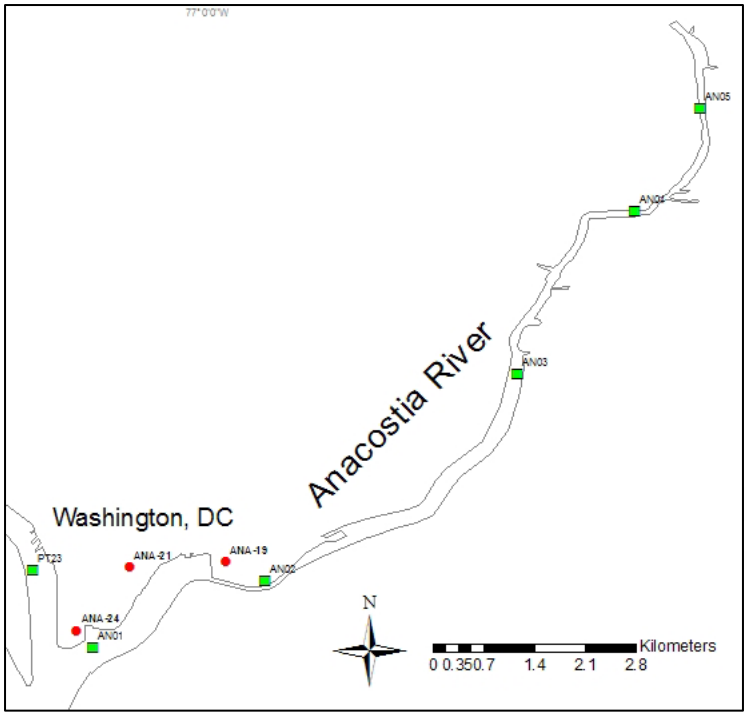
Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

(D'Elia et al 1986; Fisher et al 1992) during late spring - fall, with light and P-limitation during winter and early spring. High summer sediment P releases may prevent P-limitation during this period of the year. Sediment total chlorophyll-a values averaged 84 mg m^{-2}, slightly higher than the median value of the full flux data set. These values were about half those routinely observed in more enriched systems. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be good indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 209 mV, a value indicating generally oxidized sediments. However, Eh values were elevated at sites with very low ammonium and phosphorus fluxes, consistent with the conceptual model guiding these analyses.

5-1H. Anacostia River

Location and General Description

The Anacostia River estuary is a small tributary to the tidal Potomac River in the immediate vicinity of Washington, DC. This is a highly polluted and degraded tidal freshwater estuary (Fig. 3-1 and 5-8; Table 3-1) This urban estuary has a surface area of about 3.3 km^2 and an average depth of 4.3 m and much greater depths associated with



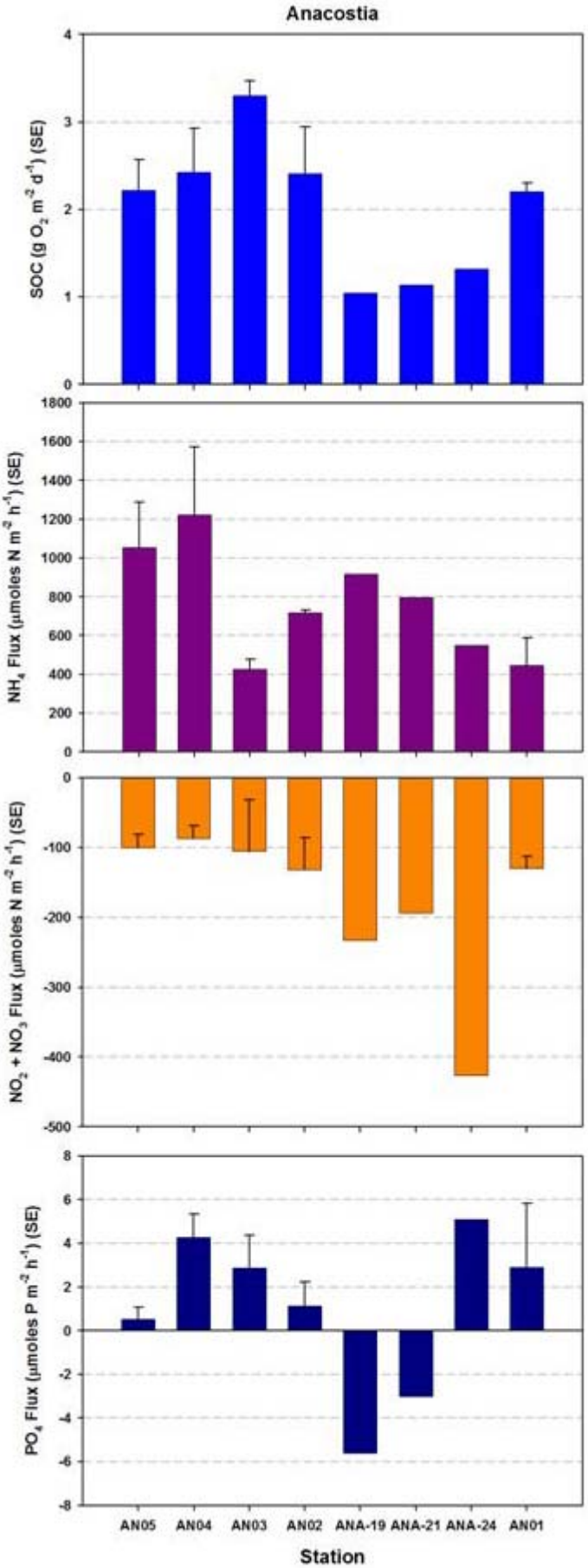


Figure 5-8a. *Map of upper Chesapeake Bay showing Anacostia River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

limited navigation channels. The nominal nitrogen loading rate is 120 g N m^{-2} yr^{-1}. This rate is very high compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Anacostia watershed is truly urban (49%) with about 23% impervious surfaces. Natural vegetation and cultivated land make up 31% and 17% of the land area, respectively. Wetlands constitute less than 2% of the watershed. During the period when flux measurements were made (2002) there were strong indications of persistent hypoxic bottom waters at some sites and these conditions can have strong influences on sediment biogeochemistry.

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 1.0 to 3.3 g O_2 m^{-2} day^{-1} and tended to be higher in the upper than lower reaches of the estuary

(Fig. 5-8a). There were several sets of low SOC values recorded in the estuary (Sta. ANA19-ANA24) and these were associated with low bottom water DO concentrations (Table 5-8). In these cases measurements of SOC were likely limited by low DO concentrations. Low SOC measurements at these sites do not indicate low levels of sediment (organic matter) metabolism. In hypoxic and anoxic sediments anaerobic metabolism is very likely clipping along at very high rates (Roden and Tuttle 1993; Marvin-DiPasquale et al 2003). Aside from the DO-limited sites, SOC in the Anacostia was high and averaged about 2.5 g O_2 m^{-2} day^{-1}. Rates of this magnitude exceed 85% on all other SOC measurements in the data set. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 8 days, a moderately short turnover time. Such a short turnover time suggest an important role for sediment processes and a potentially dynamic DO regime. The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) would have a value of about 13 if normal Redfield organic matter (e.g., phytoplankton with C:N:P = 106:16:1) was being remineralized. At most sites in the Anacostia River this ratio was much below Redfield proportions, indicating that both aerobic and anaerobic remineralization was taking place with little or no coupled sediment nitrification-denitrification. Ratios of O:N sediment flux at sites in the Anacostia River ranged from about 3 to 21 and were close to or slightly above Redfield proportions at only two sites in the estuary (Sta. AN03 and AN01). While O:N sediment flux ratios in the vicinity of 13 can be explained as remineralization of phytoplanktonic debris, flux ratios well below 13 require a different explanation. Our interpretation of these is that ammonium is being primarily generated from anaerobic metabolism, mainly based on methane production (not sulfate reduction in the Anacostia river because of the very low SO4 concentrations in tidal freshwater). Thus, in oxygen poor zones there is little to no SOC but high rates of anaerobic metabolism generating large amounts of ammonium and hence very low O:N flux ratios. Sediment ammonium fluxes were extremely high throughout the estuary and extremely large in the upper portions (1000-1200 µmol N m^{-2} hr^{-1}). Ammonium fluxes in the Anacostia River ranked 1st in magnitude of the 13 Bay and tributary sites considered in this section. It is unlikely that sufficient light reached the bottom in this system for sediment ammonium to be used by sediment autotrophs. For example, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.4 to 0.8 m (average of 0.6 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the estuary.

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were all directed into sediments along the axis of the estuary and the magnitude of flux ranged from modest (e.g., ~ 100 µmol N m^{-2} hr^{-1}) at several sites to very large (>200 - 100 µmol N m^{-2} hr^{-1}) in the lower estuary. The fact that these fluxes were directed into sediments was more than expected given the modest levels of NO_3 in the water column (Table 5-8). This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. In the case of the Anacostia River estuary there was a very strong relationship between water column nitrate concentration and sediment nitrate flux (Fig. 5-8b). At most locations in Chesapeake Bay sediment nitrate fluxes are small, especially compared to ammonium fluxes. However, in the Anacostia nitrate flues were very large. About 96% of all nitrate fluxes measured in Chesapeake Bay were lower than those measured in the Anacostia.

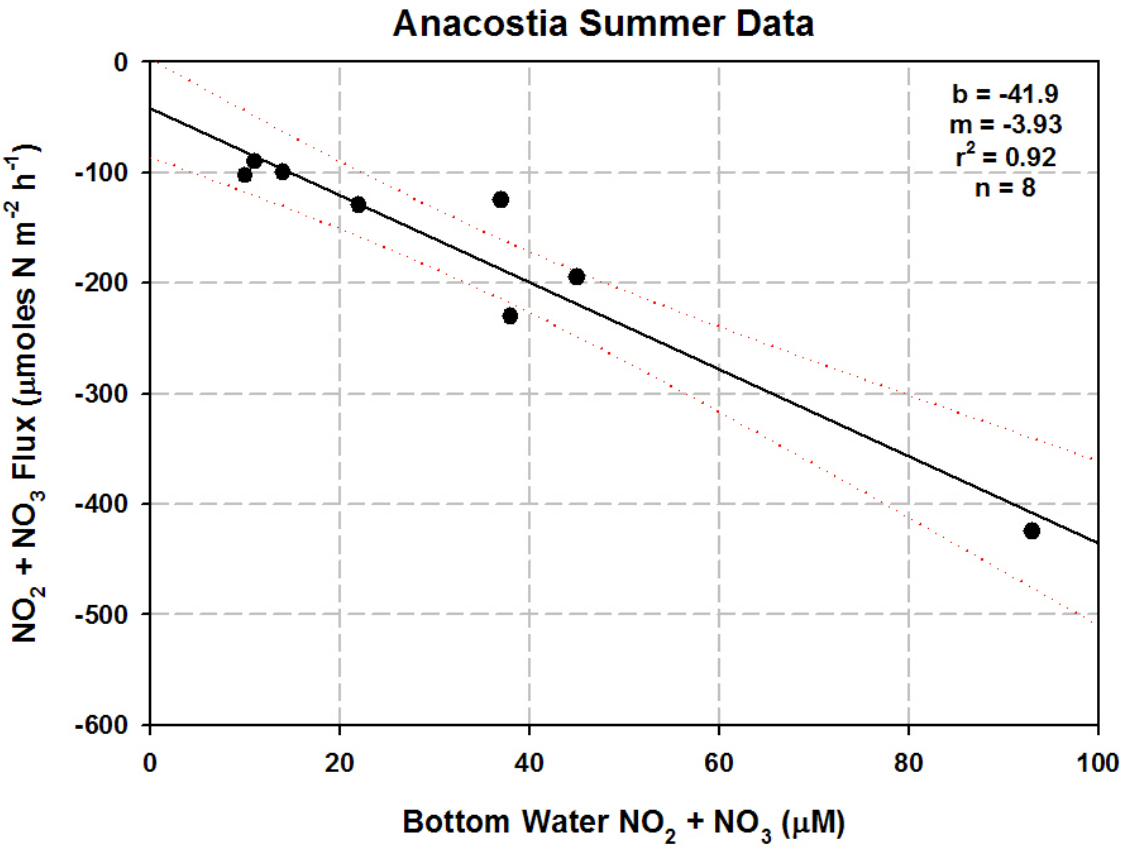


***Figure 5-8b**. Scatter plot of summer mean bottom water NO_2+NO_3 concentrations versus summer mean sediment NO_2+NO_3 flux in the Anacostia River. Results of linear regression analysis is also provided.*

Sediment phosphorus flux ranged from about -6 (directed into sediments) to about 5 µmol P m^{-2} hr^{-1}. These rates are considered to be small from an impact on water column processes point of view. Given the large SOC rates and the extremely large ammonium fluxes the very small sediment P fluxes stand in stark contrast. Since the former two fluxes are based on biological activity we conclude that physical-chemical processes are responsible for the very small P fluxes. The most likely explanation is that interstitial P is adsorbed to the iron rich sediments in this estuary. To place these small sediment P fluxes in a water quality perspective, a sediment P flux of 1 µmol P m^{-2} hr^{-1} (average for the Anacostia River) could support a phytoplanktonic production rate of less than 0.1 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). Thus, the sediment P fluxes in the Anacostia River estuary can be classified as small and can be expected to have minor potential for impacting water quality conditions.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Anacostia River estuary (Table 5-8). At least during summer conditions this is a very turbid, tidal-freshwater, moderate nitrate and often hypoxic system. It would be hard to imagine N-limitation of photosynthetic processes, although light limitation is a distinct possibility. Possibly the most distinctive feature of water quality conditions was the reverse pattern of nitrate concentration. In most estuaries, nitrate concentration is highest in the headwaters and decreases downstream. However, the opposite pattern existed in the Anacostia and likely reflects low N loading

Table 5-8. Summer bottom water conditions for the Anacostia River estuary.

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
AN05	0.1 ± 0.01	3.8 ± 0.7	14 ± 4	50 ± 10	179 ± 7
AN04	0.1 ± 0.02	4.1 ± 1.3	11 ± 3	67 ± 24	238 ± 60
AN03	0.1 ± 0.02	5.8 ± 1.5	10 ± 6	53 ± 7	219 ± 30
AN02	0.1 ± 0.01	8.0 ± 0.3	22 ± 9	81 ± 17	139 ± 27
ANA-19	0 ± 0	2.0 ± 0	38 ± 0	ND	ND
ANA-21	0 ± 0	2.1 ± 0	45 ± 0	ND	ND
ANA-24	0 ± 0	4.5 ± 0	93 ± 0	ND	ND
AN01	0.2 ± 0.01	7.5 ± 0.6	37 ± 11	68 ± 9	203 ± 59

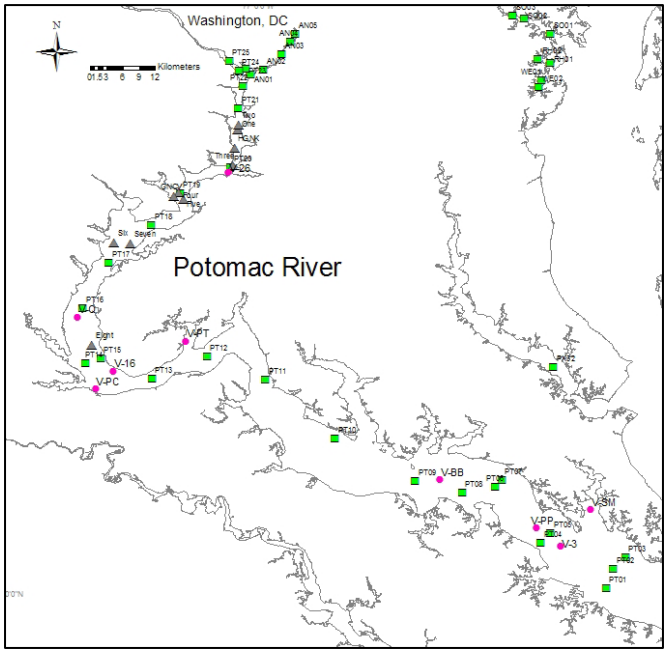
Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface
ND = No data

during a dry summer period and the influence of the mainstem Potomac River estuary which has very high nitrate concentrations in the vicinity of the mouth of the Anacostia River. Sediment total chlorophyll-a concentration averaged only 64 mg m^{-2}, below the median value of the full flux data set. The low sediment chlorophyll-a values were somewhat of a surprise given the large SOC rates and huge ammonium fluxes. However, there are other sources of organic matter in this system (e.g., surface runoff, sewage overflows and abundant streamside forest leaves) and each has some organic nitrogen associated with it. Sediment Eh values averaged 196 mV, but were highly variable in this system and at several sites data were missing because of equipment failures.

5-1I. Potomac River

Location and General Description

The Potomac River estuary, the largest tributary of Chesapeake Bay, is located on the western shore of Chesapeake Bay about half way between the Susquehanna River mouth and the Virginia capes (Fig. 3-1 and 5-9; Table 3-1). This estuary is about 158 km in length, has a surface area of 1210 km^2 and an average depth of about 6 m. The



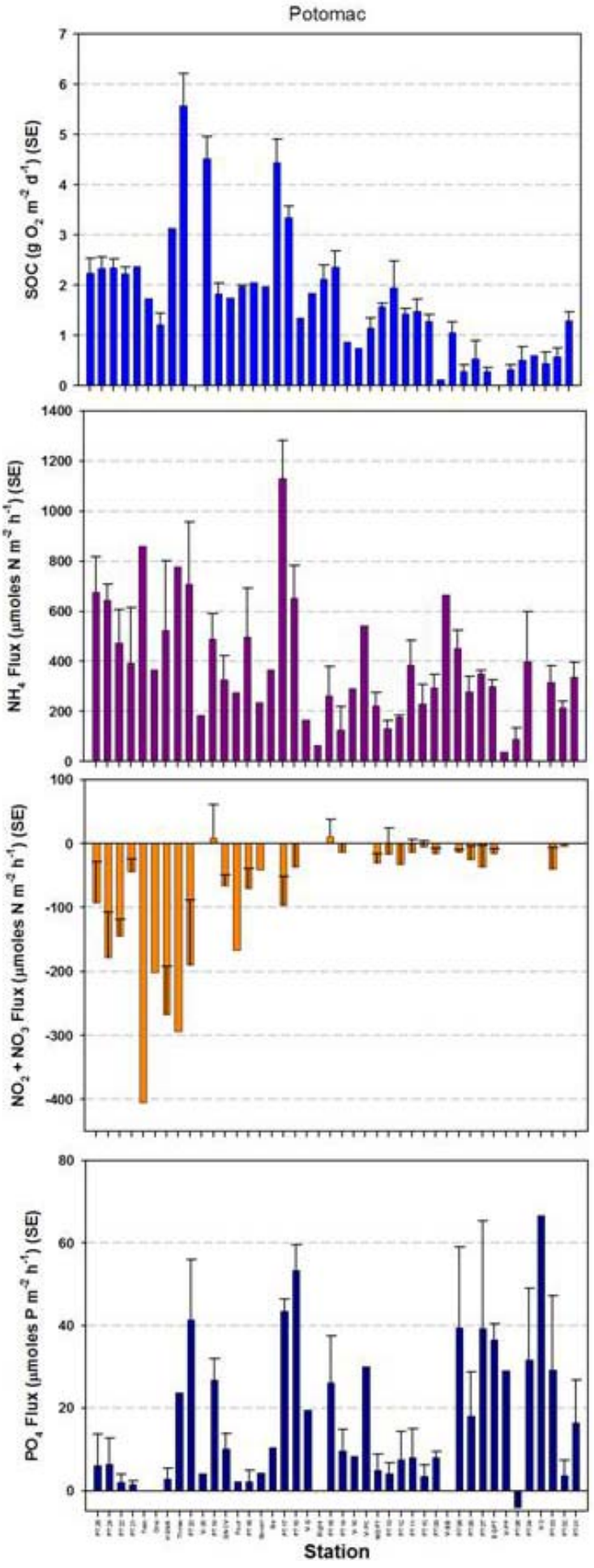


Figure 5-9. *Map of upper Chesapeake Bay showing Potomac River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

nominal nitrogen loading rate is 35 and g N m^{-2} yr^{-1}. This rate is higher than those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}, Boynton et al 1995) but are considerably less than loads to the most enriched areas of the Bay (e.g., Patapsco River estuary). Land use in the Potomac watershed is primarily natural vegetation (59 %), followed by agriculture (32%), and developed land. During the period when flux measurements were made (many years: 1979; 1985-1996; 2002; 2004) there were clear indications of chronic hypoxic bottom waters in the mesohaline portion of the estuary, and diel scale hypoxia was present in shallow areas and in tributary creeks. Sediment flux measurements in this estuary are very numerous and span the salinity gradient from tidal freshwater to the mesohaline region of the estuary.

<u>Spatial Pattern and Magnitude of Sediment Flux</u>

SOC rates ranged from about 0.1 to 5.5 g O_2 m^{-2} day^{-1} although values at most

stations were between 1 and 2 g O_2 m^{-2} day^{-1} (Fig. 5-9). SOC rates in the Potomac ranked 7th of the 13 estuaries considered in this section. There were several sets of low SOC values recorded in the estuary, all at deep sites in the lower mesohaline zone (e.g., Sta. RGPT, PT05, PT03, PT02 and PT01) and all of these were associated with low (<2 mg l^{-1}) bottom water DO concentrations (Table 5-9). In these cases SOC rates were limited by DO concentrations. Low SOC measurements at these sites do not indicate low levels of sediment (organic matter) metabolism. In hypoxic and anoxic sediments anaerobic metabolism is very likely clipping along at very high rates (Roden and Tuttle 1993; Marvin-dePasqualle et al 1998, 2003). In the mesohaline Potomac River estuary, sulfate-based anaerobic respiration is likely the major form of metabolism. The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (phytoplankton organic matter with C:N:P = 106:16:1) is being metabolized to ammonium, water and carbon dioxide. At sites in the Potomac this ratio varied a great deal, ranging from about 1 to about 74. However, there was a reasonably clear pattern along the axis of the estuary. First, most sites in the upper and middle estuary had flux ratios close to those expected for Redfield decomposition. Higher flux ratios were almost exclusively associated with very shallow sites along the flanks of the estuary. Flux ratios at or below Redfield proportions were from deeper sites mainly located in the oxygen poor waters of the lower estuary. As indicated earlier, generally high O:N flux ratios suggest missing nitrogen and that N was likely denitrified in sediments (Boynton and Kemp 1985). This pattern suggests that in those sites (shallow sites, for example) where sediments remain well oxidized because of a short and well-mixed water column, coupled nitrification-denitrification is active through the summer months. In contrast, at deeper sites that experience hypoxia during summer O:N flux ratios indicate simple remineralization of N to ammonium with no loss to denitrification. In cases where the O:N flux ratio is well below the expected 13, we suggest some additional N may have come from sulfate-based anaerobic respiration. The important management point here is that if DO in bottom waters can be elevated (>3 mg l^{-1}) a good deal of N that is now recycled many times during the warm months and supports additional phytoplankton blooms, would be effectively removed from the system via denitrification. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 13 days, not a very short turnover time. However, if we consider just the portion of the water column beneath the seasonal pycnocline, the turnover time is reduced by about a factor of two.

Sediment ammonium fluxes were variable along the main axis of the Potomac but, with the exception of several sites, quite high (> 300 µmol N m^{-2} hr^{-1}(Fig. 5-9)). Ammonium fluxes in this estuary ranked 4th of the 13 Bay and tributary sites considered in this section. Sediments in this estuary had a mean Eh = 137mV but were also quite variable; in the upper estuary sediment Eh was about 200mV, higher (up to 400 mV) in the middle estuary and generally much lower (<50 mV) in the deep waters of the lower estuary. Ammonium fluxes also tended to follow a pattern along the axis of the estuary wherein fluxes were highest in the upper estuary, reduced in the middle reaches and higher in the lower estuary. At those stations with reduced ammonium fluxes, Eh values were elevated indicating persistently oxidized sediments (e.g., in the middle portions of the estuary). This suggests that coupled denitrification - denitrification may well have been operative, consistent with lower sediment ammonium releases at these sites in the

estuary. In the lower estuary, which has chronic hypoxia during summer, denitrification was likely absent. Jenkins and Kemp (1984) reported a lack of sediment nitrification-denitrification in deeper waters of the Patuxent during summer, because of a lack of dissolved oxygen needed to support nitrification and that mechanism is likely operative in the deep areas of the mesohaline Potomac as well. Thus, the generally high fluxes in the lower estuary may represent efficient recycling of N from sediments with no shunt to denitrification. The high ammonium fluxes of the upper Potomac are particularly interesting. This area is relatively shallow, making it more likely that organic matter produced in the water column will get to the bottom rather than be metabolized in the water column (see Chapter 7), has intense algal blooms and these may provide ample labile substrate to support large sediment ammonium releases. In addition, this area of the Potomac has dense communities of the invasive clam, Corbicula sp. Some clam bed biomass estimates reach > 100 gAFDW m^{-2}. Biomass estimates in this range (higher than in almost all other areas of the Bay) could have direct and indirect influences on ammonium flux. Clams could bioturbate the sediments thereby stimulating microbial activity and enhance ammonium flux. In addition, direct excretion of ammonium by clams would also contribute to this flux. Both may combine to produce these very large ammonium fluxes. It is possible that sufficient light reached the bottom in this system and some ammonium was being used by sediment autotrophs. There are substantial SAV beds along the shoreline of the upper Potomac although we never obtained sediment cores from within these macrophyte communities. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.5 to 2.1 m (average of 1.1 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were mainly directed into sediments along the axis of the estuary, decreasing from very large fluxes in the upper estuary to very small fluxes in the lower estuary (Fig. 5-9). Nitrate plus nitrite fluxes ranged from -410 to 5 µmol N m^{-2} hr^{-1}. Fluxes into sediments were likely in response nitrate in the water column (Table 5-9). During summer in the Potomac nitrate concentrations ranged from 100 µM in the upper estuary to less than 1 µM in the mesohaline zone and sediment nitrate flux generally followed this pattern with highest fluxes into sediments in the upper estuary and much smaller fluxes in the lower estuary (Fig. 5-9b). This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. We would suggest that much of this nitrate is denitrified but we have no direct measurements of this process. It would be quite useful to work towards having a denitrification measurement methodology that could be readily incorporated into sediment monitoring programs such as those described here. It is interesting to note that there were very few sites (2) in all of the Potomac where nitrate was evolved from sediments; nitrate being released by sediments is a sign of surficial sediment nitrification, an index we use to indicate good sediment quality. In this enriched and high nitrate estuary sediments may be supporting nitrification where conditions are appropriate, but sediment uptake of nitrate from the water column obscures this process.

Perhaps the most interesting aspect of sediment flux in the Potomac relates to phosphorus (Fig. 5-9). Sediment phosphorus flux ranged from about -5 to 65 µmol P m^{-2} hr^{-1}, rates that are generally considered to be modest to large from an impact on water column processes point of view. Sediment P fluxes averaged about 21 µmol P m^{-2} hr^{-1} in the Potomac. A sediment P flux of this magnitude could support a phytoplanktonic production rate of about 0.7 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). However, in several portions of the Potomac (oligohaline and hypoxic mesohaline portions) sediment phosphorus fluxes were closer to 50 µmol P m^{-2} hr^{-1} and these would support much higher rates of primary production (~1.5 g C m^{-2} day^{-1}). The fact that P flux at all but one site in the Potomac River were from sediments to the water column was interesting. We believe there are three mechanisms operating to cause these large rates. In the tidal freshwater portion pH values can be elevated during daylight periods (> 9.5) and has been observed to get as high as 10.5. At pH values greater than 9.0 phosphorus can be released into solution from sorption sites on iron-rich sediment particles. Bailey et al (2006) reported on a series of experiments that demonstrated this pH effect in the Potomac. Second, there is a clear increase in P flux in the vicinity of the salt wedge (~PT17) and this may represent a common ion effect or some other process in the release of P from sediments. Finally, in the mesohaline portions of the estuary experiencing hypoxic conditions sediment P flux is again large. This is likely caused by the release of P from iron hydroxides when they react with reduced S compounds. Thus, in one estuary with a large salinity gradient we see all three mechanisms thought to control P release from estuarine sediments.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Potomac River estuary (Table 5-9). At least during summer conditions the upper estuary is a very turbid, well mixed, high DO, and high nitrate system. Nitrogen limitation of photosynthetic processes would be hard to imagine as nitrate concentrations remain high, even in summer. Sediment Eh conditions are generally quite positive (>200mV) and sediment chlorophyll-a concentrations are modest. In the lower estuary water transparency is much greater and phytoplankton N-limitation occurs (Fisher et al 1992). However, deep waters are seasonally hypoxic and sediment Eh values indicate reduced conditions which are consistent with large sediment ammonium and phosphorus fluxes and very low sediment O:N flux ratios. We would predict much lower sediment N and P fluxes if DO and Eh conditions improved in the mesohaline portion of this estuary.

Table 5-9. *Summer bottom water conditions for the Potomac River estuary.*

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
PT25	0.2 ±0	5.5 ±1.0	21 ± 15	60 ± 3	293 ± 21
PT24	0.2 ±0	7.8 ±0.6	35 ± 13	58 ± 16	175 ± 24
PT22	0.2 ±0	7.5 ±1.2	75 ± 6	69 ± 1	210 ± 6
PT21	0.2 ±0	6.5 ±0.5	84 ± 3	88 ± 14	218 ± 33
Two	0.2 ±0	6.4 ±0	94 ± 0	83 ± 0	ND
One	0.2 ±0	6.2 ±0	90 ± 0	83 ± 0	ND
HGNK	0 ± 0	8.5 ±0.2	100 ± 9	15 ± 2	ND
Three	0.2 ±0	6.4 ±0	74 ± 0	69 ± 0	ND
PT20	0.2 ±0	8.5 ±1.2	62 ± 8	100 ± 18	171 ± 18
V-26	ND	ND	ND	ND	ND
PT19	0.2 ±0.1	8.5 ±0.7	37 ± 16	65 ± 2	161 ± 29
GNCV	0 ± 0	10.5 ± 0.6	54 ± 6	14 ± 0.1	ND
Four	0.2 ±0	7.1 ±0	60 ± 0	62 ± 0	ND
PT18	0.5 ±0.2	6.4 ±0.6	31 ± 15	83 ± 17	102 ± 7
Seven	0.1 ±0	8.0 ±0	35 ± 0	66 ±0	ND
Six	0.1 ±0	9.6 ±0	26 ± 0	83 ± 0	ND
PT17	1.4 ±0.7	6.1 ±0.4	30 ± 9	78 ± 7	156 ± 71
PT16	1.9 ±0.8	5.9 ±0.2	30 ± 8	92 ± 14	250 ± 67
V-Q	ND	ND	ND	ND	ND
Eight	1.8 ±0	7.4 ±0	16 ± 0	59 ± 0	ND
PT15	4.3 ± 1.6	6.1 ±0.5	27 ± 12	50 ± 4	381 ± 15
PT14	3.1 ± 1.3	7.0 ±0.3	32 ± 14	61 ± 3	337 ± 44
V-16	ND	ND	ND	ND	ND
V-PC	ND	ND	ND	ND	ND
MDPT	5.4 ±0.7	5.0 ±0.3	32 ± 7	75 ± 12	218 ± 58
PT13	6.4 ± 1.6	5.8 ±0.5	11 ± 3	59 ± 4	326 ± 34
PT12	8.7 ±0.8	5.1 ±0.1	15 ± 6	53 ± 4	265 ± 77
PT11	11.4 ± 0.6	4.2 ±0.3	6 ± 2	83 ± 5	172 ± 74
PT10	13.6 ± 0.9	6.1 ±3.0	1 ± 1	79 ± 15	197 ± 111
PT09	15.2 ± 1.0	2.4 ±0.7	1 ± 0.5	96 ± 5	149 ± 89
V-BB	ND	ND	ND	ND	ND
PT08	14.6 ± 1.4	3.7 ±1.9	1 ± 0.3	88 ± 12	166 ± 51
PT06	18.7 ± 0.7	0.9 ±1.3	2 ± 2	78 ± 10	82 ± 153
PT07	18.3 ± 0.7	0.9 ±0.6	1 ± 1	86 ± 6	58 ± 161
RGPT	15.7 ± 0.5	0.6 ±0.2	3 ± 1	100 ± 12	17 ± 24
V-PP	ND	ND	ND	ND	ND
PT05	19.6 ± 0.6	0.9 ±0.6	3 ± 2	59 ± 5	231 ± 54
PT04	18.0 ± 1.5	1.6 ±1.3	1 ± 0	80 ± 6	6 ± 104
V-3	ND	ND	ND	ND	ND
PT03	19.9 ± 0.6	1.0 ±1.2	2 ± 1	80 ± 13	40 ± 144
PT02	19.8 ± 0.3	1.3 ±1.1	0.4 ±0	70 ± 7	18 ± 105
PT01	16.7 ± 1.1	3.5 ±1.2	1 ± 1	89 ± 4	170 ± 143

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface
ND = No data

5-1J. Pocomoke River

Location and General Description

The Pocomoke River estuary is located at the southern eastern shore portion of Chesapeake Bay (Fig. 3-1 and 5-10; Table 3-3). This substantial eastern shore estuary has a surface area of about 6.9 km^2 and an average depth of about 2.7 m. Nominal nitrogen loading rate is 6 g N m^{-2} yr^{-1}. This rate is low compared to those delivered to the Maryland mainstem Bay (21 and 1 g N m^{-2} yr^{-1}). Land use in the Pocomoke watershed is primarily agricultural (45%) followed by natural vegetation (26%). There is very little (1%) developed land. During the period when flux measurements were made (1980-1981 and 1999) there was no indication of hypoxic bottom waters, although diel scale hypoxia may have been present in shallow areas.

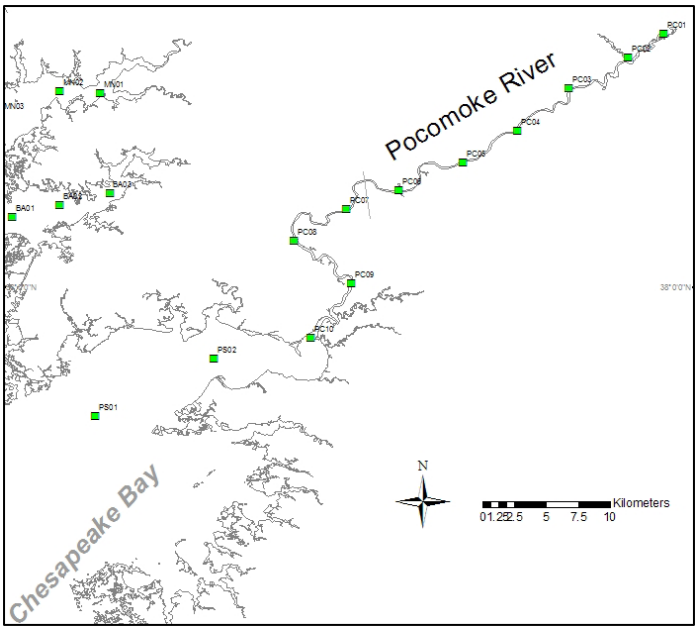
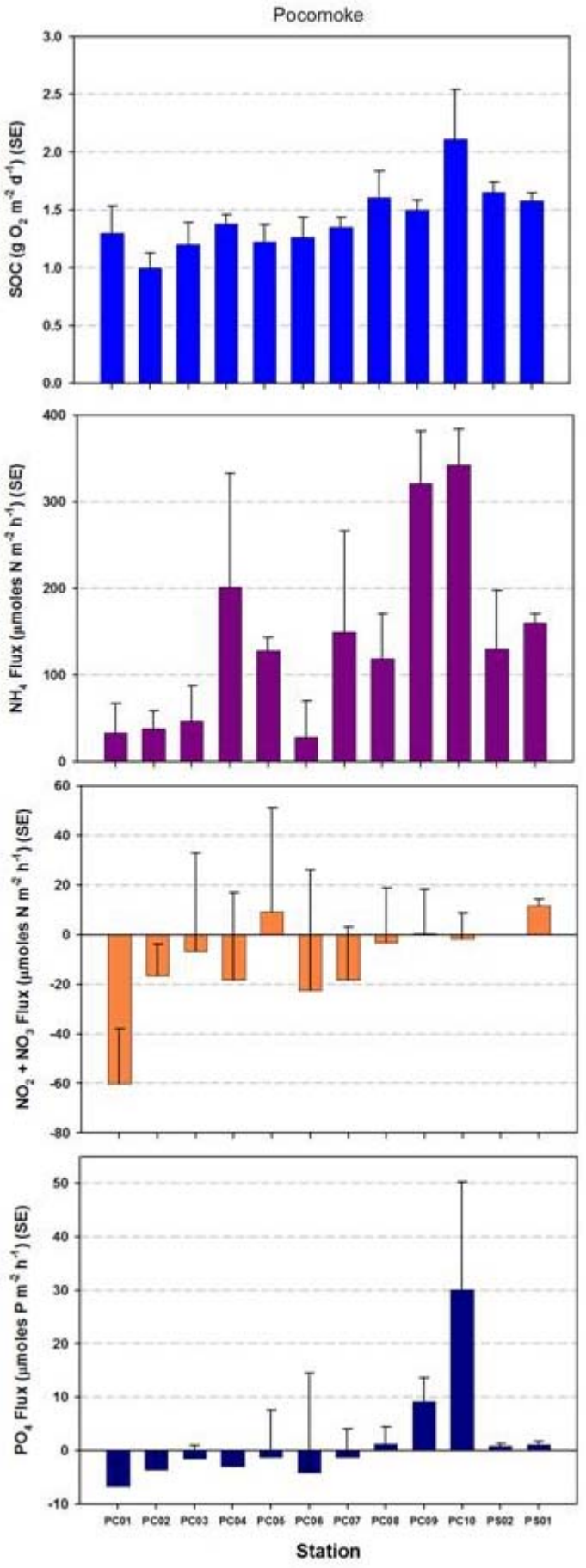


Figure 5-10. *Map of upper Chesapeake Bay showing Pocomoke River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*



Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 1.0 to 2.1 g O_2 m^{-2} day^{-1} although values at most stations were between 1.2 and 1.6 g O_2 m^{-2} day^{-1} (Fig. 5-10). These values are above the median for the full data set (1 g O_2 m^{-2} day^{-1}). There was a clear pattern of increasing SOC rates in a down estuary direction although the increase was not large. The fact that rates were similar among stations and modest in magnitude may be related to the fact that DO was relatively high in bottom waters at all stations (in sharp contrast to DO conditions in some other tributaries) and thus not limiting SOC rates at any location. The associated environmental variable data set also suggests modest sediment chlorophyll-a concentration (below the median for the full data set, 72 mg m^{-2}) and a lack of clear increases or decreases along the axis of the estuary. As described earlier, the ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) would have a value of about 13 if normal Redfield organic matter (e.g., phytoplankton with C:N:P = 106:16:1) was being remineralized. At all sites in the Pocomoke River this ratio was close to or well above 13, indicating that some remineralized N was lost and may have been denitrified. Ratios of O:N sediment flux at sites in the Pocomoke ranged from about 13 to 97. Sediment Eh values (198 mV) in this estuary were also above the median (177 mV) for the full data set and these conditions would be appropriate for coupled nitrification-denitrification to occur. Dissolved oxygen turnover time based on SOC as the only DO sink (water column DO stock divided by SOC) is about 9 days, a modest turnover time suggesting moderate influence of SOC on water column DO conditions.

Sediment ammonium fluxes tended to increase from the head of the estuary proceeding downstream (Fig. 5-10). However, with a few exceptions (PC09 and PC10) ammonium fluxes were small (<150 µmol N m^{-2} hr^{-1}) throughout the estuary. Ammonium fluxes in the Pocomoke ranked 9th of the 13 Bay and tributary sites discussed in this section. The Pocomoke is one of the few "dark water" rivers in the Maryland portion of the Bay. Because of this, phytoplankton activity in these dark waters is limited and DOC levels (natural) are among the highest in the Bay. It is likely that much of this DOC is refractory material. Thus, small ammonium fluxes may be related to a limited supply of labile organic matter at the sediment surface. As the estuary broadens, and there is more marine influence near the mouth, light conditions improve and plankton production increases providing more labile material for sediment processes. The higher ammonium flux down estuary may be caused by these processes. Sediments in this estuary appear to be well oxidized (average Eh = 198 mV) and there was no indication in this data set of persistent summertime deep water hypoxia. This suggests that coupled denitrification - denitrification may well have been operative, consistent with low sediment ammonium releases. It is also possible that sufficient light reached the bottom in the more saline portion of this system and ammonium was being used by sediment autotrophs. However, secchi disk measurements made along the axis of the estuary indicate secchi depths ranging from 0.35 to 0.9 m (average of 0.55 m) and these suggest that 1 % of light does not reach the sediment surface at average depths in this estuary. Some sediment autotrophic activity is possible along the flanks of this shallow system, especially near the mouth, and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were generally small (<20 µmol N m^{-2} hr^{-1}) and directed both into and out of sediments along the axis of the estuary. In

general, nitrate flux was directed into sediments in proportion to nitrate concentration in the overlying water, but there were exceptions to this pattern. The fact that these fluxes were not all directed into sediments was expected given the lower concentrations of NO_3 in the water column (Table 5-10). This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. It is quite possible that sediment nitrification rates at several stations were sufficiently high to reduce the gradient in NO_3 concentrations between the water column and sediments thus reducing the magnitude of NO_3 flux. It is, however, clear that sediment nitrification was taking place at several stations because NO_3 was escaping, at small rates, from sediments to the water column and this, in itself, is an indication of well oxidized sediments.

Sediment phosphorus flux ranged from about -7.0 to 30 µmol P m^{-2} hr^{-1}, but all but two sites exhibited fluxes less than 2 µmol P m^{-2} hr^{-1} and at 7 of 11 sites P was moving from the water to sediments. These rates are small from an impact on water column processes point of view. For example, a sediment P flux of 2 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of less than 0.1 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at most sites in the Pocomoke River were into sediments was interesting. In several tidal freshwater sites P fluxes tend to be in this direction (e.g., Anacostia River). The two larger sediment P fluxes observed in the Pocomoke (Sta. PC09 and PC10) were associated with a rapid increase in salinity (Table 5-10). There was no other clear suggestion in the environmental data to explain these higher fluxes.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Pocomoke River estuary (Table 5-10). During summer conditions this is a relatively turbid estuary with a strong salinity and nitrate gradient. It would be hard to imagine N-limitation of photosynthetic processes in the upper estuary but P and light limitation are distinct possibilities. It is useful to note that water column nitrate concentrations exhibited the expected pattern of sharp decrease along the axis of the estuary. Sediment total chlorophyll-a values averaged 51 mg m^{-2}, slightly below the median value of the full flux data set. These values were less than half those routinely observed in more enriched systems. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be excellent indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 198 mV, a value indicating oxidized sediments, and an indication, along with high bottom water DO concentrations and occasional NO_3 fluxes to the water from sediments, that sediment nitrification-denitrification was an active process.

Table 5-10. Summer bottom water conditions for the Pocomoke River estuary.

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
PC01	0.1 ± 0	4.5 ± 0.7	27 ± 8	32 ± 4	149 ± 50
PC02	0.1 ± 0	4.5 ± 0.6	27 ± 8	38 ± 2	143 ± 37
PC03	0.1 ± 0	4.5 ± 0.3	26 ± 9	27 ± 3	231 ± 7
PC04	0.1 ± 0	5.0 ± 0.2	24 ± 11	62 ± 23	214 ± 31
PC05	0.2 ± 0	5.2 ± 0.2	23 ± 11	61 ± 10	241 ± 4
PC06	1.1 ± 0.8	4.9 ± 0.4	27 ± 7	38 ± 9	210 ± 11
PC07	3.5 ± 2.1	4.9 ± 0.3	23 ± 9	40 ± 9	240 ± 13
PC08	4.8 ± 2.6	4.7 ± 0.3	19 ± 9	37 ± 6	239 ± 15
PC09	8.5 ± 2.3	4.4 ± 0.3	9 ± 4	74 ± 9	226 ± 46
PC10	12.2 ± 2.0	5.2 ± 0.4	3 ± 2	70 ± 7	204 ± 39
PS02	19.7 ± 0.9	6.5 ± 0.1	0 ± 0	74 ± 13	154 ± 58
PS01	19.1 ± 0.9	6.3 ± 0.1	1 ± 0	62 ± 3	122 ± 61

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface

5-1K. York River

Location and General Description

The York River estuary is located on the western shore of the Virginia sector of Chesapeake Bay and is one of several major western shore tributaries (Fig. 3-1 and 5-11; Table 3-3). This estuary is about 92 km in length, has a surface area of 215 km^2 and an average depth of about 4.3 m. Land use in the York watershed is primarily natural vegetation (68%), followed by agriculture (21%), and developed land (2.2%). During the period when flux measurements were made (1978, 1983, 1988, 1990, 1992-1994, 1996) there were no indications of chronic hypoxic bottom waters in the mesohaline portion of the estuary where flux measurements were conducted. The mouth of the York River estuary has a well described spring-neap tidal cycle of low and high DO conditions in deep water but this was not captured in the environmental data associated with flux measurements. Diel-scale hypoxia was likely present in shallow areas and in tributary creeks. The York River data were not collected by the Boynton Lab; the York is the only system in this synthesis where all data were collected by other researchers. As a result, not all of variables were collected and station locations were not distributed as in many of the Maryland tributaries. In particular, flux stations in the York were segregated into deep and shallow sites and this separation is noted in the graphics in this section. Measurements made in the York included those made in the dark as well as under ambient light conditions. Only dark fluxes were included here to be consistent with the rest of the flux data base.

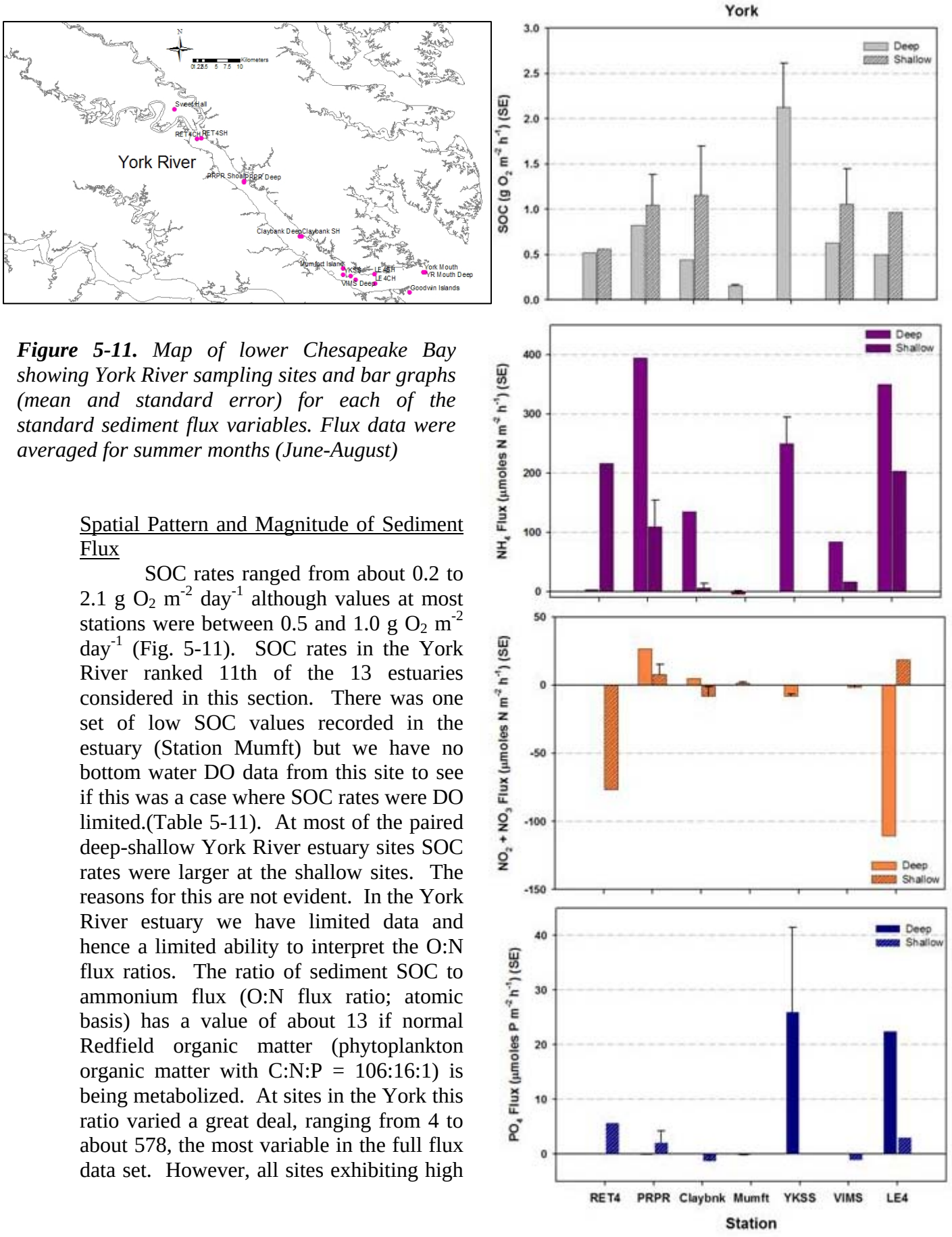


Figure 5-11. *Map of lower Chesapeake Bay showing York River sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August)*

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 0.2 to 2.1 g O_2 m^{-2} day^{-1} although values at most stations were between 0.5 and 1.0 g O_2 m^{-2} day^{-1} (Fig. 5-11). SOC rates in the York River ranked 11th of the 13 estuaries considered in this section. There was one set of low SOC values recorded in the estuary (Station Mumft) but we have no bottom water DO data from this site to see if this was a case where SOC rates were DO limited.(Table 5-11). At most of the paired deep-shallow York River estuary sites SOC rates were larger at the shallow sites. The reasons for this are not evident. In the York River estuary we have limited data and hence a limited ability to interpret the O:N flux ratios. The ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (phytoplankton organic matter with C:N:P = 106:16:1) is being metabolized. At sites in the York this ratio varied a great deal, ranging from 4 to about 578, the most variable in the full flux data set. However, all sites exhibiting high

O:N flux ratios were from shallow or reasonably shallow (< 6 m) sites. However, some shallow sites also exhibited low O:N flux ratios and this was unexpected. Flux ratios at or below Redfield proportions were mainly from sites deeper than 6 m. As indicated earlier, generally high O:N flux ratios suggest missing nitrogen and that N was likely denitrified in sediments (Boynton and Kemp 1985) or utilized by sediment autotrophs. This pattern suggests that in those sites (shallow sites, for example) where sediments remain well oxidized because of a short and well-mixed water column, coupled nitrification-denitrification is active through the summer months. In contrast, at deeper sites that experience hypoxia during summer O:N flux ratios indicate simple remineralization of N to ammonium with no loss to denitrification. However, DO conditions in deep waters of the York River at the time of flux measurements were not very hypoxic. In cases where the O:N flux ratio is well below the expected 13, we suggest some additional N may have come from sulfate-based anaerobic respiration. However, we have no measurements of anaerobic metabolism in this or most other tributaries. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 29 days, a very long turnover time. However, if we consider just the portion of the water column beneath the seasonal pycnocline, the turnover time is reduced by about a factor of two and still represents a relatively long turnover time.

Sediment ammonium fluxes were variable along the main axis of the York but quite high at a few deep sites (> 300 μmol N m^{-2} hr^{-1}; Fig. 5-11). Ammonium fluxes in this estuary ranked 11th of the 13 Bay and tributary sites considered in this section. No Eh data were available for the York River so we have no direct measure of the redox condition of sediments. It is also possible that sufficient light reached the bottom in this system and ammonium was being used by sediment autotrophs. Some sediment autotrophic activity is possible along the flanks of this system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005). Ammonium flux was generally smaller at shallow sites and this is consistent with autotrophic utilization of ammonium.

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were directed both into and out of sediments along the axis of the estuary (Fig. 5-11). Nitrate plus nitrite fluxes ranged from -105 to 22 μmol N m^{-2} hr^{-1}. Large nitrate flux into sediments occurred at two sites having high nitrate concentrations in the water column. This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. However, at other sites in the estuary nitrate was being released or consumed by sediments, but rates were very small.

Sediment phosphorus flux ranged from about -1 to 25 μmol P m^{-2} hr^{-1}, rates that are generally considered to be small from an impact on water column processes point of view. Sediment P fluxes averaged about 4 μmol P m-2 hr-1 in the York. A sediment P flux of this magnitude could support a phytoplanktonic production rate of about 0.1 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P flux at most sites in the York River were small was interesting;

there was apparently not enough hypoxia in these waters to promote P flux from these sediments except possibly at the deepest sites where DO may be low.

Environmental Conditions

Very little environmental data were available from the sites where sediment flux measurements were conducted. With the exception of the most up estuary and down estuary sites, nitrate concentrations were low, as expected. Bottom water DO concentrations were not especially low, even in deep waters. No sediment Eh or chlorophyll-a data were available (Table 5-11).

Table 5-11. Summer bottom water conditions for the York River estuary.

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
RET4$_d$	12.6	4.7	0	ND	ND
RET4$_s$	9.6	4.4	38	ND	ND
PRPR$_d$	14.4	5.1	1.5	ND	ND
PRPR$_s$	16 ± 1.7	6.3 ± 0.2	1.3 ± 0.4	ND	ND
Claybnk$_d$	18.2	5.7	1.9	ND	ND
Claybnk$_s$	19.3 ± 1.8	6.3 ± 0.2	1.5 ± 1.0	ND	ND
Mumft	17.2 ± 0.0	ND	5.7 ± 4.9	ND	ND
YKSS	18.5 ± 1.3	ND	0.8 ± 0.3	ND	ND
VIMS$_d$	18.8	6.0	1.0	ND	ND
VIMS$_s$	21.3 ± 1.5	6.3 ± 0.2	0.6 ± 0.1	ND	ND
LE4$_d$	23.5	3.5	12	ND	ND
LE4$_s$	20.8	8.1	3.0	ND	ND

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface
s = shallow (shoal area)
d = deep (channel area)
If no SE listed, sample size is N = 1
ND = No data

5-1L. Mainstem Chesapeake Bay

Location and General Description

The Chesapeake Bay mainstem (Fig. 3-1 and 5-12; Table 3-3) has a surface area of 5820 km^2 and an average depth of about 8.9 m. The nominal nitrogen loading rate is about 21 g N m^{-2} yr^{-1} (Boynton et al 1995) but this varies by about a factor of two between dry and wet years. Land use in the full Chesapeake watershed (64,000 mi^2) is primarily natural vegetation (63 %), followed by agriculture (29%), and developed land (3.6%). During the period when flux measurements were made (many years: 1980, 1985-1998) there were clear indications of chronic hypoxia and anoxia in bottom waters in the

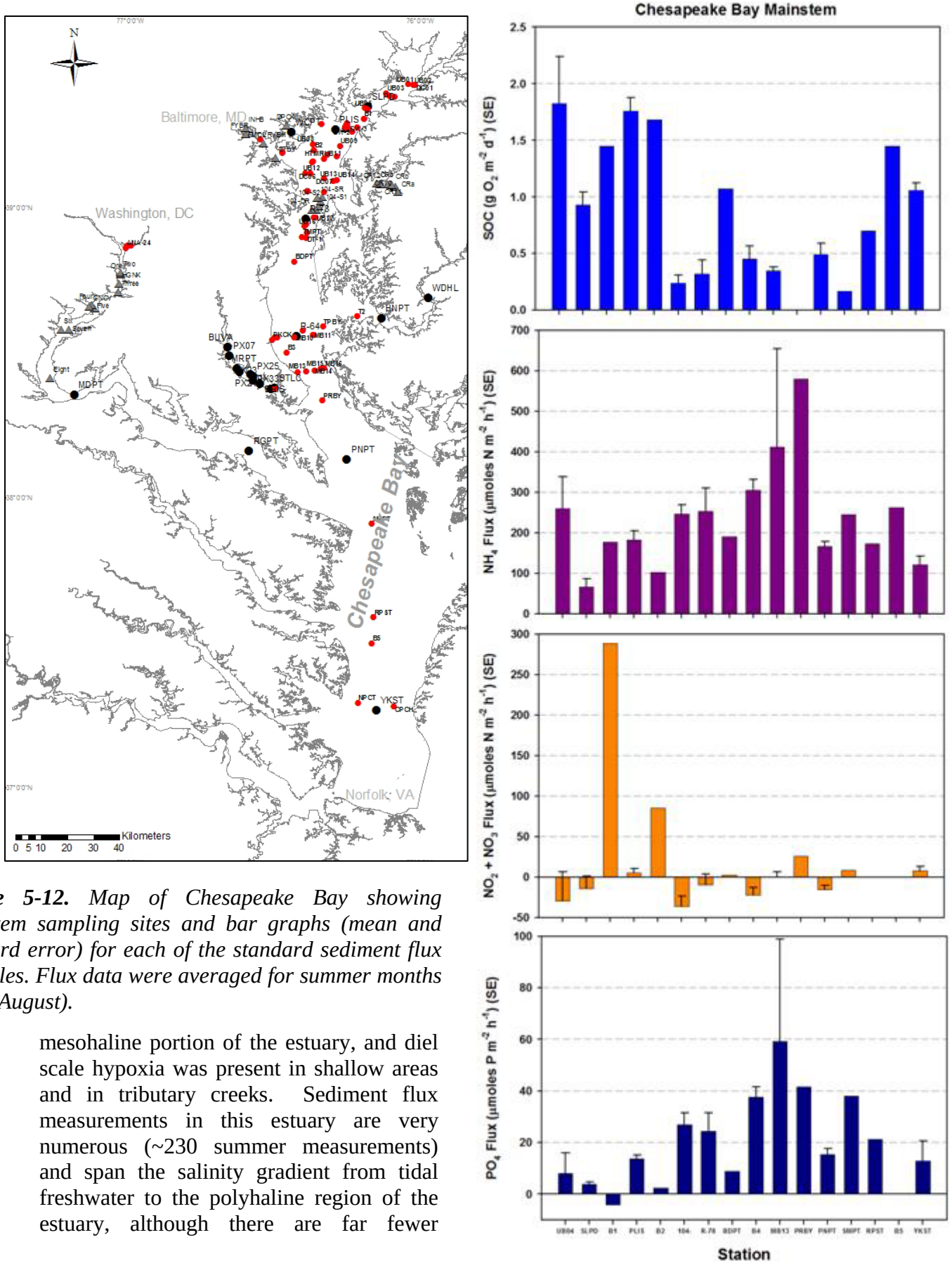


Figure 5-12. *Map of Chesapeake Bay showing mainstem sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August).*

mesohaline portion of the estuary, and diel scale hypoxia was present in shallow areas and in tributary creeks. Sediment flux measurements in this estuary are very numerous (~230 summer measurements) and span the salinity gradient from tidal freshwater to the polyhaline region of the estuary, although there are far fewer

measurements available in the southern Bay.

Spatial Pattern and Magnitude of Sediment Flux

SOC rates during summer ranged from about 0.2 to 1.8 g O_2 m^{-2} day^{-1} and were quite variable along the main axis of the Bay (Fig. 5-12). SOC rates in the Chesapeake mainstem ranked 10^{th} of the 13 estuaries considered in this section. The main longitudinal pattern evident in the flux data was a trend towards highest values in the upper Bay, low values in the mid-Bay and intermediate values in the lower Bay. In general, highest SOC rates were measured at relatively shallow sites (< 8 m), mainly in the upper Bay. There were many sets of low SOC values recorded in the mid-Bay region, all at deep sites in the mesohaline zone (e.g., Sta. 104 through SMPT) and all of these were associated with low (<2 mg l^{-1}) bottom water DO concentrations (Table 5-12). In these cases, measurements of SOC were limited by DO concentrations. Low SOC measurements at these sites do not indicate low levels of sediment (organic matter) metabolism. In hypoxic and anoxic sediments anaerobic metabolism is very likely clipping along at very high rates (Roden and Tuttle 1993; Marvin-dePasqualle et al 1998, 2003). In the mid-Bay, sulfate-based anaerobic respiration is likely the major form of metabolism. The ratio of summer season sediment SOC to ammonium flux (O:N flux ratio; atomic basis) has a value of about 13 if normal Redfield organic matter (phytoplankton organic matter with C:N:P = 106:16:1) is being metabolized to ammonium, water and carbon dioxide. At sites in the Chesapeake mainstem this ratio varied a great deal, ranging from about 2 to about 157. However, there was a reasonably clear pattern along the axis of the estuary. First, only sites in the upper and lower estuary had flux ratios well above those expected for Redfield decomposition. Higher flux ratios were exclusively associated with relatively shallow sites having well oxygenated bottom waters. Flux ratios at or below Redfield proportions were from deeper sites mainly located in the oxygen poor waters of the mid and lower estuary. As indicated earlier, generally high O:N flux ratios suggest missing nitrogen and that N was likely denitrified in sediments (Boynton and Kemp 1985). This pattern suggests that in those sites (shallow sites, for example) where sediments remain well oxidized because of a short and well-mixed water column, coupled nitrification-denitrification is active through the summer months. In contrast, at deeper sites that experience hypoxia during summer O:N flux ratios indicate simple remineralization of N to ammonium with no loss to denitrification. In cases where the O:N flux ratio is well below the expected 13, (e.g., Sta. 104 in very deep water just south of Annapolis, MD) we suggest some additional N may have come from sulfate-based anaerobic respiration. The important management point here is that if DO in bottom waters can be elevated (>3 mg l^{-1}) a good deal of N that is now recycled many times during the warm months and supports additional phytoplankton blooms during the summer period, would be effectively removed from the system via coupled nitrification-denitrification. Dissolved oxygen turnover time based of SOC as the only DO sink (bottom water column DO stock divided by SOC) is about 15 days, not a very short turnover time.

Sediment ammonium fluxes exhibited a very clear pattern along the main axis of the Bay, with modest rates in the upper Bay (mean < 150 µmol N m^{-2} hr^{-1}), increasing rates through the mid Bay region (250 to 575 µmol N m^{-2} hr^{-1}) and intermediate rates in the lower Bay (mean = 200 µmol N m^{-2} hr^{-1}; (Fig. 5-12). Ammonium fluxes for the full

axis of the mainstem Bay ranked 8th of the 13 Bay and tributary sites considered in this section. If just the mesohaline, mid-Bay were considered the ranking would be 2nd or 3rd of the 13 locations considered in this section. Sediments in the mainstem Bay had a mean Eh = 32mV but were also quite variable; in the upper estuary sediment Eh was much higher (103 - 265 mV), very low (negative) in the mid Bay and higher at the Bay mouth. Ammonium fluxes also tended to follow an inverse of the sediment Eh pattern along the axis of the estuary wherein fluxes were lowest in the upper estuary, large in the middle reaches and moderate in the lower estuary. At those stations with reduced ammonium fluxes, Eh values were elevated indicating persistently oxidized sediments (e.g., in the upper Bay). This suggests that coupled denitrification - denitrification may well have been operative, consistent with lower sediment ammonium releases at these sites in the estuary. In the mid Bay, which has chronic hypoxia during summer, denitrification was likely absent. Jenkins and Kemp (1984) reported a lack of sediment nitrification-denitrification in deeper waters of the Patuxent during summer, because of a lack of dissolved oxygen needed to support nitrification and that mechanism is likely operative in the deep areas of the mainstem Bay as well. Thus, the generally high fluxes in the mid Bay represent efficient recycling of N from sediments (as ammonium) with no shunt to denitrification. It is possible that sufficient light reached the bottom in this system and some ammonium was being used by sediment autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from about 0.5 (upper Bay) to 2.4 m (lower bay; average of 1.4 m) and these suggest that much less than 1 % of light reaches the sediment surface at the average depth of the estuary. Nevertheless, some sediment autotrophic activity is possible along the flanks of this system and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005).

Sediment nitrite plus nitrate (NO_2 + NO_3) fluxes were, with only two exceptions, small (<35 μmol N m^{-2} hr^{-1}) and directed either into or out of sediments (Fig. 5-12). Nitrate plus nitrite fluxes ranged from -35 to 280 μmol N m^{-2} hr^{-1}, but all but two ranged between -35 and 25 μmol N m^{-2} hr^{-1}. Fluxes into sediments were likely in response to nitrate in the water column (Table 5-12), although the pattern here is not nearly as clear as it was in other tributary rivers. This pattern has been observed elsewhere (e.g. Boynton and Kemp 1985; Cowan and Boynton 1996) and has been interpreted as a gradient-driven flux. We would suggest that much of this nitrate is denitrified but we have no direct measurements of this process. It would be quite useful to work towards having a denitrification measurement methodology that could be readily incorporated into sediment monitoring programs such as those described here. It is interesting to note that there were very few sites (4) in all of the mainstem Bay where nitrate was evolved from sediments; nitrate being released by sediments is a sign of surficial sediment nitrification, an index we use to indicate good sediment quality. If management actions are able to relieve the chronic hypoxia and anoxia of deep waters we would predict that many more sites would be showing signs of sediment nitrification.

Perhaps the most interesting aspect of sediment flux in the Chesapeake mainstem relates to phosphorus (Fig. 5-12). Sediment phosphorus flux ranged from about -3 to 60 μmol P m^{-2} hr^{-1}, rates that are generally considered to be modest to large from an impact on water column processes point of view. Sediment P fluxes averaged about 19 μmol P m^{-2} hr^{-1} in the Chesapeake mainstem and this flux ranks 6th among the 13 sites

considered in this section. A sediment P flux of this magnitude could support a phytoplanktonic production rate of about 0.6 g C m-2 day-1, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in most enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). However, in several portions of the Chesapeake mainstem (hypoxic mesohaline portions) sediment phosphorus fluxes were closer to 50 µmol P m^{-2} hr^{-1} and these would support much higher rates of primary production (~1.5 g C m^{-2} day^{-1}). The fact that P flux at all but one site in the mainstem Bay were from sediments to the water column was interesting. We believe there are several mechanisms operating to cause these large rates. In the tidal

Table 5-12. Summer bottom water conditions for the Chesapeake Bay Mainstem.

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
UB04	0.8 ± 0.3	6.0 ± 0.2	72 ± 3	71 ± 23	133 ± 64
SLPD	3.6 ± 0.5	5.7 ± 0.3	49 ± 7	68 ± 10	176 ± 35
B1	4.8 ± 0.0	5.9 ± 0.0	20 ± 0	ND	ND
PLIS	4.8 ± 0.5	7.4 ± 0.2	30 ± 3	86 ± 13	265 ± 30
B2	6.8 ± 0.0	5.7 ± 0.0	7.6 ± 0	ND	ND
104	14.3 ± 0.7	1.0 ± 0.3	4.7 ± 1.6	275 ± 31	103 ± 26
R-78	16.6 ± 0.7	0.7 ± 0.3	3.8 ± 2.5	94 ± 9	5 ± 30
BDPT	13.2 ± 0.0	4.3 ± 0.0	1.7 ± 0.0	172 ± 0	37 ± 0
B4	18.0 ± 0.5	0.9 ± 0.3	2.4 ± 0.8	102 ± 12	-14 ± 22
MB13	13.3 ± 0.5	0.7 ± 0.3	0.5 ± 0.2	103 ± 40	-32 ± 64
PRBY	19.2 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	160 ± 0	-195 ± 0
PNPT	18.3 ± 0.6	1.7 ± 0.3	3.4 ± 0.9	84 ± 11	37 ± 28
SMPT	22.5 ± 0.0	0.1 ± 0.0	0.4 ± 0.0	75 ± 0	-63 ± 0
RPST	24.0 ± 0.0	1.8 ± 0.0	1.0 ± 0.0	96 ± 0	-93 ± 0
B5	24.0 ± 0.0	3.9 ± 0.0	0.7 ± 0.0	ND	ND
YKST	27.2 ± 1.5	6.1 ± 0.8	0.4 ± 0.1	97 ± 20	51 ± 1

Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface
ND = No data

freshwater/oligohaline portion there is a well developed infaunal community and bioturbation associated with these animals and direct excretion could account for P-fluxes across an otherwise oxidized and iron-rich sediment-water interface. In the mesohaline

portions of the estuary experiencing hypoxic/anoxic conditions, sediment P flux is much larger and this is likely caused by the release of P from iron hydroxides when they react with reduced S compounds. Thus, in one estuary with a large salinity gradient we see two different mechanisms thought to control P release from estuarine sediments.

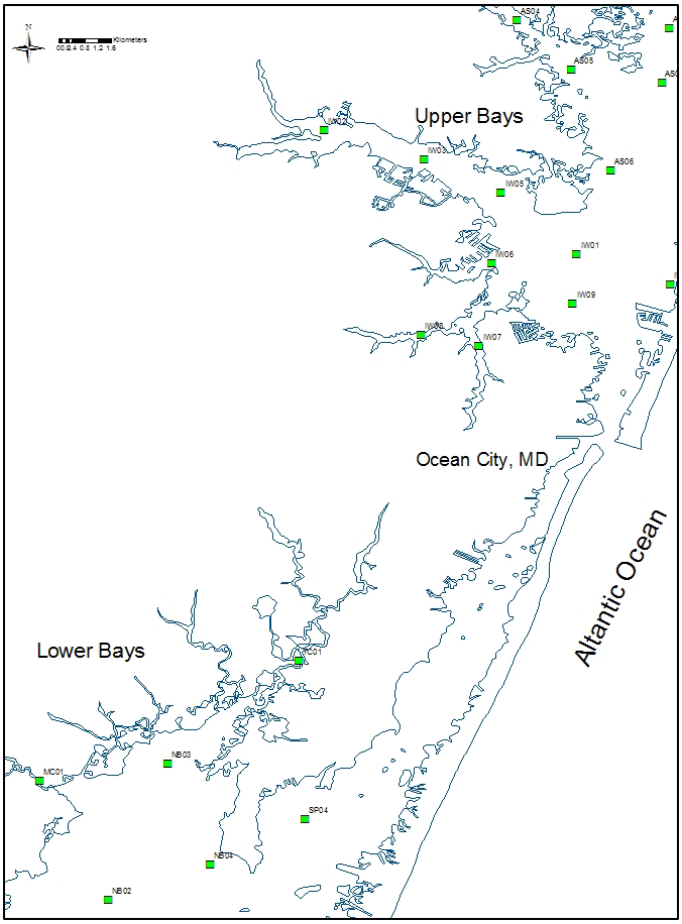
Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the mainstem Bay (Table 5-12). At least during summer conditions the upper estuary is a very turbid, well mixed, high DO, and high nitrate system. Nitrogen limitation of photosynthetic processes would be hard to imagine as nitrate concentrations remain high even in summer in the upper Bay. P-limitation and light limitation has been reported for this sector of the Bay (Fisher at al. 1992). In the mid and lower Bay N-limitation of phytoplankton production is more common. Sediment Eh conditions exhibited a strong axial gradient being high in the upper Bay, very reduced in the mid bay and moderate in the lower Bay. Eh and sediment ammonium and phosphorus fluxes followed the same axial pattern. Sediment chlorophyll-a concentrations ranged from modest in the upper and lower Bay to very large, even in summer, in the mid-Bay.

5-1M. Maryland Coastal Bays

Location and General Description

The Maryland Coastal bays are located along the Maryland Atlantic coast and are separated from the ocean by a series of barriers islands with connections to the ocean by a series of inlets (Fig. 3-1 and 5-12; Table 3-3) This lagoonal system has a total surface area of about 282 km^2 and an average depth of about 1.0 m. We have divided this lagonnal system into four portions based on inspection of sediment flux data and the geography of these systems. We combined flux stations into the following four categories: 1) Upper Tributaries including the St. Martin River and associated creeks; 2) Lower Tributaries including Newport Bay; 3) Upper Open Waters including Assawoman and Isle of Wright Bay and; 4) Lower Open which includes the Maryland portion of Chincoteague Bay. Nominal nitrogen loading rate range from 2.4 (Sinepuxent Bay) to 40 (St Martin River) g N m^{-2} yr^{-1}, with the large areas of the upper and low bays ranging from about 3 to 6 g N m^{-2} yr^{-1} (Boynton et al 1996). These rates are quite low, except for the Upper and Lower Tributaries, compared to those delivered to the Maryland mainstem Bay (21 g N m^{-2} yr^{-1}). Land use in the Coastal Bays watershed varies widely in all land use categories. For example, Chincoteagure Bay watershed has almost no urban land, 33% agricultural land, 31% forested land and 23% wetlands. At the other extreme Assawoman Bay watershed has 29% urban, 27 % agriculture, 19% forest and 24% wetland. Isle of Wright Bay watershed is similar but with less urban (18%), more agriculture (41%) and little wetland (4%). During the period when flux measurements were made (2003) there was no indication of seasonal-scale chronic hypoxic bottom waters, although diel scale hypoxia was present, especially in the Upper and Lower Tributaries (www.eyesonbay.net).



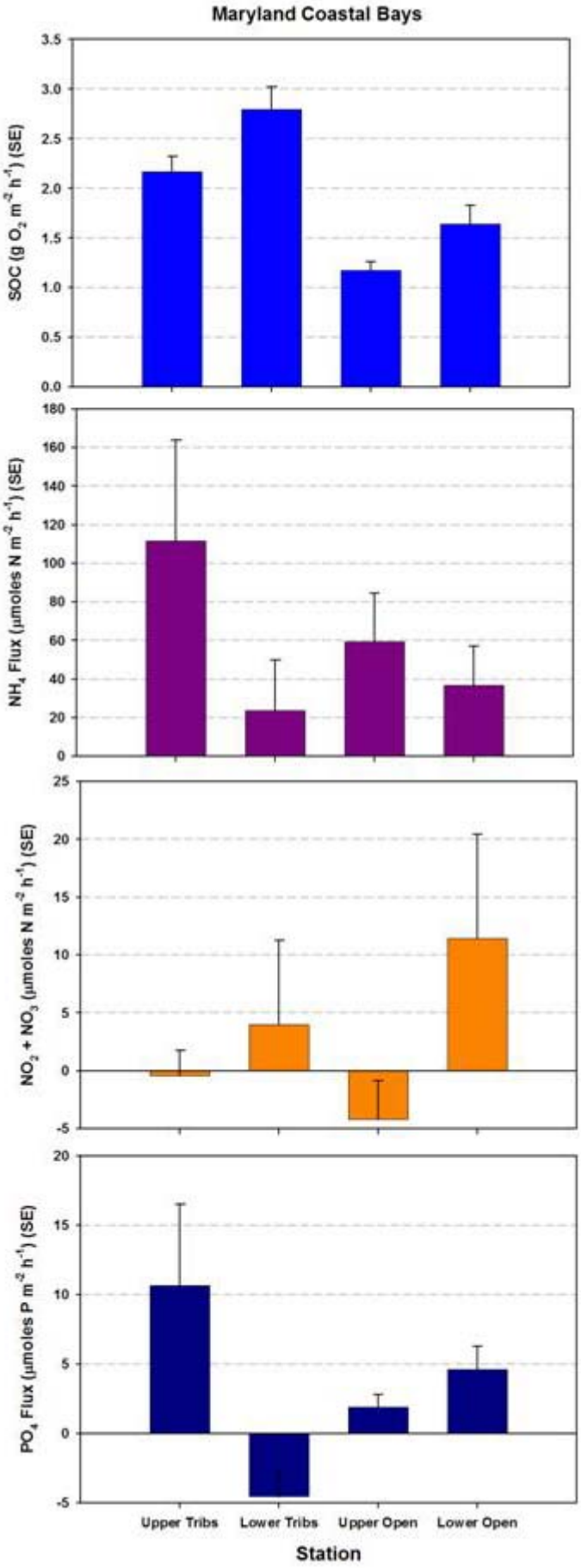


Figure 5-13. *Map of Maryland's Eastern Shore showing Coastal Bays sampling sites and bar graphs (mean and standard error) for each of the standard sediment flux variables. Flux data were averaged for summer months (June-August).*

Spatial Pattern and Magnitude of Sediment Flux

SOC rates ranged from about 1.1 to 2.7 g O_2 m^{-2} day^{-1} and were almost twice as large in the Upper and Lower Tributaries than in open Bay areas (Fig. 5-13). These rates were also well above the average rate for the entire flux data set (1.0 g O_2 m^{-2} day^{-1}). As explained earlier, the ratio of sediment SOC to ammonium flux (O:N flux ratio; atomic basis) would have a value of about 13 if normal Redfield organic matter (e.g., phytoplankton with C:N:P = 106:16:1) was being metabolized. At all sites in the Coastal Bays the ratio was far above 13, indicating that some

remineralized N was lost and may have been denitrified in sediments. Ratios of O:N sediment flux at sites in the Coastal Bays ranged from about 35 to 210. Dissolved oxygen turnover time based of SOC as the only DO sink (water column DO stock divided by SOC) is about 4 days, a short turnover time suggesting an important role for sediment SOC and a dynamic water column DO regime.

Sediment ammonium fluxes (Fig. 5-13) were highest in the Upper Tributaries and even these rates were not very high (~110 µmol N m-2 hr-1) with much smaller values associated with all the other location groups (20 - 60 µmol N m-2 hr-1; Fig. 5-13). The Maryland Coastal Bays rank 13th of 13 areas of the Bay and tributaries reported in this section. Sediments in this estuary appear to be well oxidized, especially in the Open Bays, and there was no indication in this data set of persistent summertime deep water hypoxia. This suggests that coupled denitrification - denitrification may well have been operative, consistent with low sediment ammonium releases. However, it is also possible that sufficient light reached the bottom in this very shallow system and ammonium remineralized in sediments was being used by benthic autotrophs. However, Secchi disk measurements made along the axis of the estuary indicate Secchi depths ranging from 0.2 to 0.3 m (average of 0.25 m) and these suggest that less than 1 % of light reaches the sediment surface at the average depth of the estuary. Nevertheless, sediment autotrophic activity is possible along the flanks of this shallow system, and in deeper areas when waters are even just slightly clearer (Secchi depths ~0.5 m), and might play a role in reducing sediment ammonium fluxes as suggested by Kemp et al (2005). In fact, benthic macroalgae often are abundant and could also play a role in diverting sediment N releases into autotrophic biomass.

Sediment nitrite plus nitrate ($NO_2 + NO_3$) fluxes were all very small (<12 µmol N m^{-2} hr^{-1}) and were directed both into and out of sediments (Fig. 5-13). Some of these fluxes (e.g., Upper Tributaries) were at the level of detection. The fluxes from sediment to water in the Lower Open waters indicates nitrification was taking place in sediments and this is consistent with relatively high sediment Eh and well oxygenated bottom waters.

Sediment phosphorus flux ranged from about -4 to 11 µmol P m^{-2} hr^{-1}, rates that are generally considered to be small from an impact on water column processes point of view (Fig. 5-13). For example, a sediment P flux of 10 µmol P m^{-2} hr^{-1} could support a phytoplanktonic production rate of about 0.3 g C m^{-2} day^{-1}, (based on Redfield stochiometric ratios for phytoplankton of C:N:P = 106:16:1). Phytoplanktonic production rates of 3 g C m^{-2} day^{-1} would be considered extremely high while rates greater than 1 g C m^{-2} day^{-1} would be common in enriched regions of Chesapeake Bay and tributary rivers (e.g., Harding et al 2002; Boynton et al 1982). The fact that P fluxes at most sites in the Coastal Bays were small is again consistent with oxidized sediments and with the likely possibility that autotrophs are active at the sediment-water interface.

Environmental Conditions

There were several distinctive features of water column and sediment environmental conditions in the Coastal Bays (Table 5-13). At least during summer conditions this is a turbid, high salinity, very low nitrate and non-hypoxic system. We have no information concerning N-limitation of photosynthetic processes, but it seems possible. Light limitation is a distinct possibility. Sediment total chlorophyll-a values

averaged 52 mg m^{-2}, well below the median value of the full flux data set. These values serve as an indication of the amount of labile organic matter available to support sediment fluxes and have proven to be excellent indicators of flux in other studies in Chesapeake Bay (Cowan and Boynton 1996). Sediment Eh values averaged 235 mV, a value indicating oxidized sediments, and an indication, along with high bottom water DO concentrations, that sediment nitrification-denitrification was an active process.

Table 5-13. *Summer bottom water conditions for the Maryland Coastal Bays.*

Station	Salinity$_b$	DO (mg L^{-1})$_b$	$NO_2 + NO_3$ (µM)$_b$	Sed. Chl. *a* (mg m^{-2})$_t$	Eh (mV)$_1$
Upper Tribs	24 ± 1	7.6 ± 0.4	0.25 ± 0.04	39 ± 4	187 ± 33
Lower Tribs	20 ± 1	8.4 ± 0.6	0.21 ± 0.03	70 ± 11	78 ± 61
Upper Open	26 ± 1	6.4 ± 0.2	0.30 ± 0.10	39 ± 5	312 ± 15
Lower Open	26 ± 0	7.5 ± 0.3	0.25 ± 0.04	23 ± 5	322 ± 21

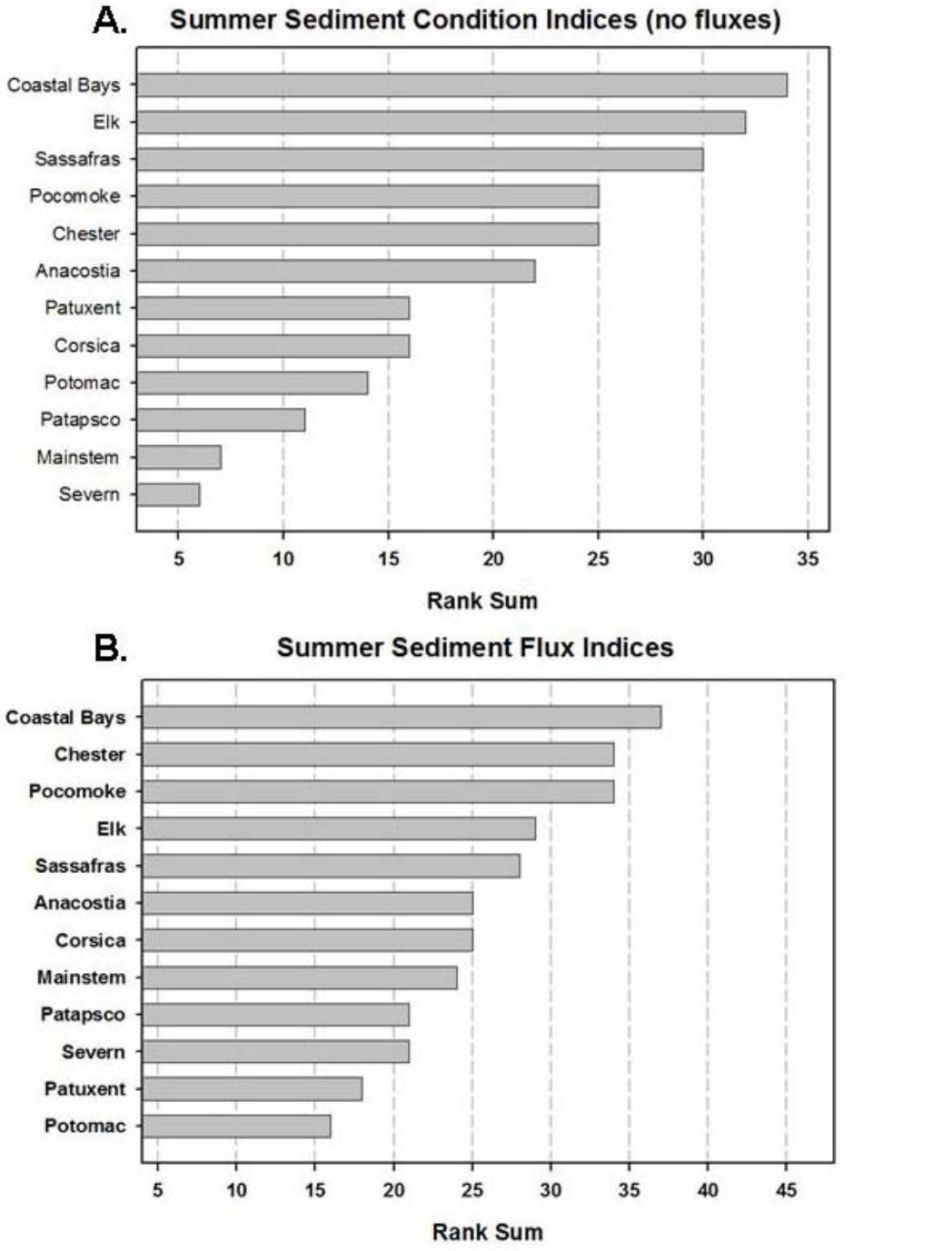
Summer (Jun-Aug) average (± SE) bottom water conditions.
b = Bottom water (0.5 m above sediment surface)
t = Total chlorophyll *a*
1 = Eh values (corrected mV) at 1 cm below sediment surface
ND = No data

5-2. "Take-Home" Summary

- Among the 13 locations summarized here there is considerable diversity in spatial patterns and magnitude of sediment fluxes. Such a result was expected given the diversity of tributaries sampled and the water and sediment quality of these systems. However, in most cases, the patterns of flux along salinity, depth, DO and sediment redox gradients largely conformed to our conceptual model of factors regulating sediment flux patterns and magnitude. Later in this report Chapters are devoted to examining, in more detail, these and other factors thought to regulate sediment flux characteristics. In most tributary and mainstem Bay sites, sediment fluxes of oxygen, N and P exerted a considerable influence on water quality conditions. It is expected that these fluxes will decrease if nutrient loading to these systems decrease.
- A summary chart of relative flux magnitude, sediment environmental conditions and sediment flux impact on water quality conditions was developed. This chart provides easy reference to all the tributary rivers, mainstem Bay and Maryland Coastal Bay sites included in this report (Table 5-14).
- We have also developed two simple indices, the first of sediment condition and the second of sediment flux magnitude (Figs 5-14a, b). The summer sediment condition index was developed by ranking each of the 12 systems considered here using summer average bottom water DO concentration, sediment Eh and sediment total chlorophyll-a concentration. The York River was excluded because we did not have sufficient sediment and deep water environmental data. The system that had the highest sediment chlorophyll-a concentration was ranked one; the system with the lowest bottom water DO was also ranked one and the system with the

lowest sediment Eh values received a ranking of one. If the same system had a ranking of one for these three sediment condition measurements the condition index would be 3. Conversely, if a system ranked 12th for all three variables the sediment condition index would be 36. With this index, the higher the score the better the sediment conditions.

- We constructed a similar index for sediment fluxes. In this case we ranked fluxes from each system from one to 12 with the highest values ranked as one and the lowest flux ranked 12. The rankings for the four fluxes (SOC + NH_4 + NO_2 and NO_3 + PO_4) were added together to obtain the summer sediment flux index. This index could range from 4 to 48. The results of this exercise suggest that sediment conditions largely predict the magnitude of sediment fluxes, at least in a relative sense, for this group of Chesapeake Bay tributaries and mainstem. For example, the Coastal Bays, Elk, Sassafras and Pocomoke Rivers rank high in terms of sediment conditions. Conversely, the Severn, mainstem Bay, Patapsco, Potomac, Corsica and Patuxent Rivers rank low in terms of sediment conditions. Other sites are intermediate. The sediment flux index closely corresponded with the sediment condition index. This result suggests that many of the important features of sediment condition and flux have been captured in these monitoring efforts. However, it is also important to remember that there are many biogeochemical feedbacks in the sediment-water system. While we indicated that sediment flux corresponds to sediment conditions, it is also true that sediment fluxes contribute to creating sediment conditions. Later in this Report we make the case that nutrient loading rates set the ultimate boundaries for sediments fluxes and sediment conditions. Furthermore, the delivery rate of organic matter to sediments, which is in turn related to nutrient loading rates (e.g., Boynton et al 1982), is a strong proximal regulator of sediment condition and flux. However, it is useful to have a simple index that provides first-order indications of sediment conditions and likely nature and magnitude of sediment fluxes.



Rank sums based on 1 = poor to 12 = good sediment condition for 12 estuaries.

A. Summer sediment condition indices based on surficial sediment chlorophyll-a, Eh and bottom water dissolved oxygen.

B. Summer sediment flux indices based on SOC, NH_4, NO_2+NO_3 and PO_4 flux. High SOC and NO_2 + NO_3 flux = good.

Figure 5-14*. Ranking of summer sediment condition (a) and summer sediment fluxes (b) for 13 Chesapeake Bay systems. Indice details are contained in the footnotes.*

Table 5-14. Mean summer rankings of sediment fluxes, sediment conditions, DO status, sediment P flux impact on primary production and SOC impact on water column DO conditions. Ranking details are contained in the footnotes.

Estuary	Sediment Flux Rate Rank SOC: lowest=1, highest=13 NH_4 and PO_4: highest=1, lowest=13 NO_2+ NO_3 = lowest positive rate = 1, highest positive rate = 13				Sediment Condition Rank Bottom Water DO: lowest=1, highest=13 Total Chl-*a*: highest=1, lowest=12 Eh: lowest=1, highest=12			Hypoxia Effects on Sediment Flux ✔= present ✔✔= severe		PO_4 Flux Production Impact (g C m^{-2} d^{-1})*	DO Turnover Time (days)**
	SOC	NH_4	NO_2 + NO_3	PO_4	DO	Total Chl-*a* (top 1 cm)	Eh (1 cm below surface)	Chronic	Diel		
Elk	9	10	3	8	11	10	11		✔	Small	11
Sassafras	3	12	6	11	13	9	8		✔	Small	27
Patapsco	6	2	13	2	3	4	4	✔✔	✔✔	Large	8 / 4
Chester	13	5	11	7	6	7	12		✔	Moderate	13
Corsica	11	3	12	1	10	1	5		✔✔	Large	3
Severn	8	7	2	5	1	3	2	✔	✔✔	Moderate	7
Patuxent	4	6	7	3	2	5	9	✔	✔	Large	16 / 8
Anacostia	12	1	1	13	8	8	6	✔	✔	Small	8
Potomac	5	4	4	4	5	6	3	✔✔	✔	Moderate / Large	13 / 6
Pocomoke	7	9	9	12	7	11	7		✔	Small / Moderate	9
York	1	11	5	10	9	No data	No data		✔	Small	29 / 15
Mainstem Chesapeake Bay	2	8	10	6	4	2	1	✔✔	✔	Moderate / Large	15 / 17
Maryland Coastal Bays	10	13	8	9	12	12	10		✔	Small	4

Bad (1) and Good (12 to 13) condition rank based on estuaries with data for each variable.
* Based on mean summer PO_4 Flux. Whole estuary/regions of higher PO_4 flux. Primary production rates (g C m^{-2} d^{-1} < 0.3 = small, 0.3-0.7 = moderate and > 0.7 = large.
** Based on applicable river locations (see text for full description). Full water column turnover time/sub-pycnocline turnover time.

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Chapter 6

Seasonal Characteristics and Factors Controlling Sediment-Water Fluxes

6-1. Background

In this Chapter we examine the flux data base for seasonal patterns and flux magnitude and then begin an analysis of factors influencing flux pattern and magnitude. This analysis begins using the entire flux data set to see if patterns are robust (i.e., do patterns emerge even when a large and diverse set of measurements are considered). The analysis continues with flux data sorted by salinity zone and concludes with several focused analyses wherein extensive measurements from single systems are used to examine factors influencing sediment fluxes

6-2. Seasonal Patterns of Sediment Flux (by month)

As we indicated earlier a large percentage of the measurements contained in the flux data base were collected during summer periods (June - August) because earlier experience indicated that sediment processes are most active during these months. About 72 % of all measurements were made during the summer period (Fig. 6-1). However, there were sediment flux measurements made during the spring (11 %) and fall (12 %) and a few measurements during winter (5 %). Thus, while the summer season is emphasized there are sediment flux data available for every month of the year.

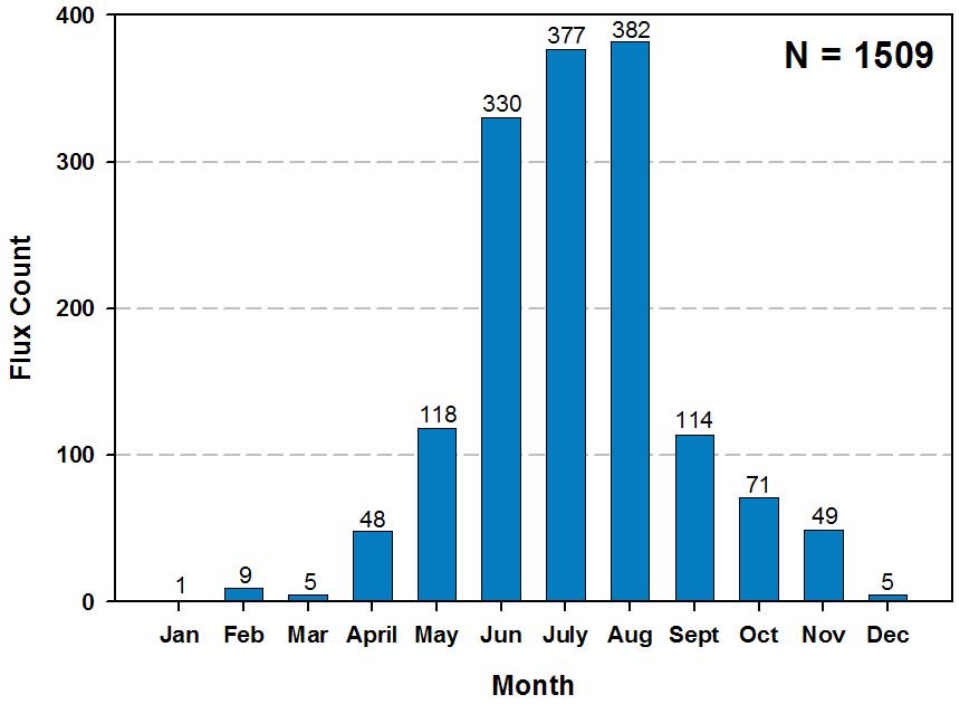

Figure 6-1*. Histograms of measured fluxes by month in Chesapeake Bay and tributary rivers.*

All of the routinely measured flux variables (SOC, NH_4, PO_4 and NO_2 + NO_3) exhibited very clear and strong seasonal patterns (Fig. 6-2). In all cases the magnitude of fluxes was lowest during the winter season and largest during either spring or summer.

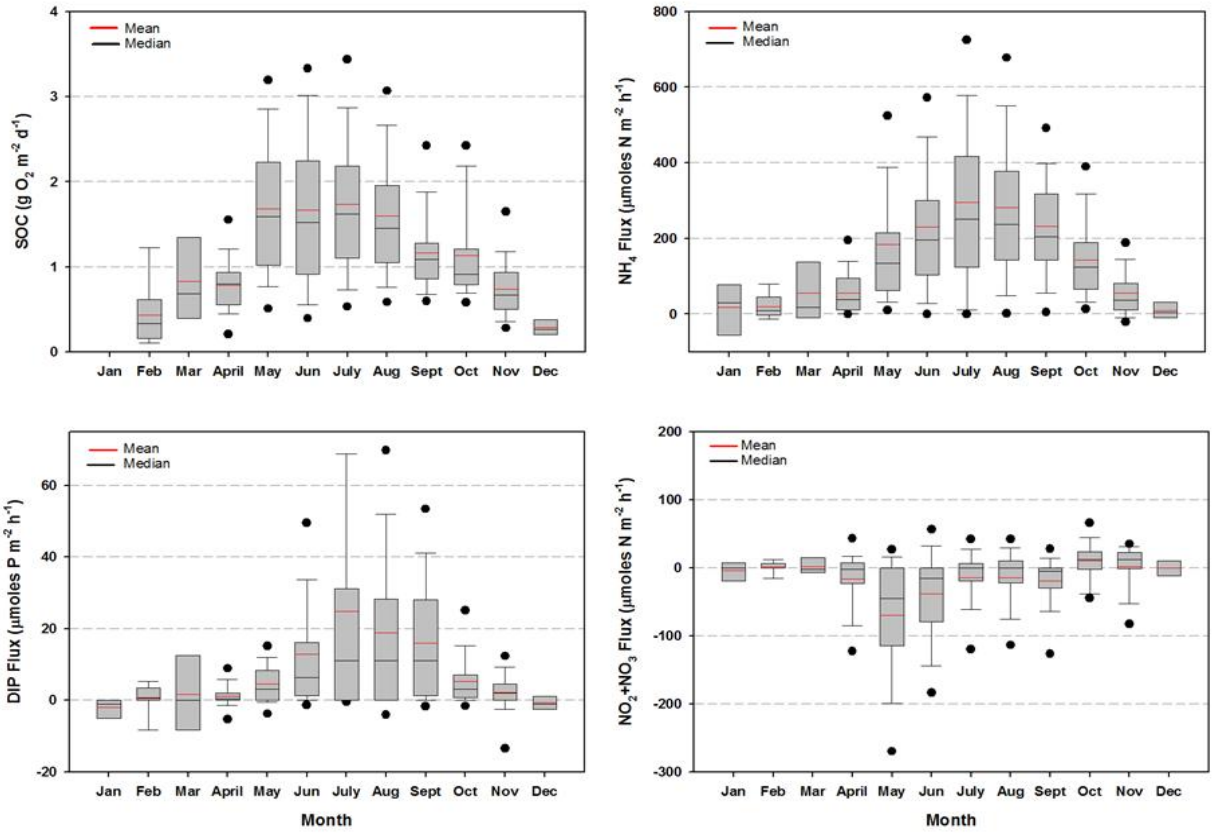

Figure 6-2. *Box and whisker plots of SOC, sediment NH_4, PO_4 and NO_2 + NO_3 fluxes by month. All Chesapeake Bay data were included in these plots. Vertical boxes include 50 % of observations, the vertical lines include 90 % of observations and the black dots encompass the remaining 10% of observations. Mean and median in each bar are indicated by red and black horizontal lines, respectively.*

During the course of a year median SOC rates ranged from about 0.3 to 1.6 g O_2 m^{-2} day^{-1} and were generally high from May - August. It is interesting to note, as we have in many previous reports (e.g., Cowan and Boynton 1996), that SOC rates increase rapidly during spring. Even in this large and diverse data set median SOC rates increased sharply between April (0.8 g O_2 m_{-2} day^{-1}) and May (1.5 g O_2 m^{-2} day^{-1}). This abrupt increase is likely due to several factors. First, the annual spring diatom bloom, which occurs in most mesohaline regions of the Bay, generally sinks to the bottom during May, a bit earlier in some years and later in others (Boynton and Kemp 1985; Stankelis et al 1999). Thus, there is on the sediment surface a rich supply of labile organic matter available for decomposition. It is also during this spring period that water temperature increases rapidly, stimulating both bacterial and metazoan metabolic rates. It is likely that the combination of these two factors stimulates SOC rates during this time.

Sediment NH_4 fluxes also increased from winter to summer and then decreased during the fall to low winter levels (Fig. 6-2). Median fluxes ranged from about 10 in winter to over 250 µmol m^{-2} hr^{-1} during summer. However, there was no indication of a sharp increase in NH_4 fluxes during spring as observed for SOC. Rather, there was a gradual increase to peak fluxes in July and then a steady decline in flux magnitude through the fall. One obvious issue arises here and that concerns the fate of N associated with this decomposition. More organic matter is remineralized (as indicated by SOC rates) than N released from sediments (as indicated by NH_4 fluxes) during the spring (May) period. While we have no direct evidence for N fate we can make a stochiometric argument that indicates that some portion of this "missing" N is eventually denitrified in surface sediments via coupled nitrification - denitrification. If labile phytoplanktonic organic matter is being remineralized to CO_2 and NH_4, then the ratio of sediment oxygen consumption to NH_4 production is about 13:1 (molar basis). For example, if we use an SOC rate of 1.6 g O_2 m^{-2} day^{-1} we would expect an ammonium flux of about 320 µmol m^{-2} hr^{-1}, given these assumptions. However, median sediment NH_4 flux during May was only about 140 µmol N m^{-2} hr^{-1}. Thus, about 180m µmol N m^{-2} hr^{-1} is unaccounted. It seems likely that this N was first nitrified and then denitrified in near-surface sediments. Jenkins and Kemp (1984) and Cornwell (unpublished data) reached the same conclusion using direct measurements of denitrification. Boynton and Kemp (1985) observed the same flux behavior based on a far smaller number of measurements made in the mainstem Bay and several tributary rivers. If this scheme is true it has major implications for water quality. In brief, if surficial sediments were to remain oxidized through the summer period, then coupled nitrification - denitrification would remain active. A result of this would be that summer ammonium fluxes would also decrease and thus the supply of recycled nutrients available to phytoplankton (and for bloom formation) would also decrease. Boynton et al (1995) estimated about 25% of all N entering Chesapeake Bay was denitrified. This is about half the rate of removal reported by Seitzinger (1988) for estuaries not having severe hypoxic conditions.

Sediment fluxes of PO_4 also exhibited a seasonal pattern similar to that of NH_4 with low values predominating for all months except June - September. Median fluxes of PO_4 ranged from slightly less than zero (i.e., directed from water into sediments) during winter and early spring to about 15 µmol P m^{-2} hr^{-1} during July - September. Thus, in this very aggregated analysis, sediment fluxes of P were modest and restricted to summer months. Stochiometric ratios of median sediment N and P fluxes exhibited a strong trend during the May to September period wherein ratios were quite high (~57) in May relative to those expected for complete decomposition of phytoplanktonic organic matter (expected N:P = 16:1) and decreased steadily to about Redfield proportions (~16) for August and September. It may be that oxidized sediments prevented P release during the spring and early summer because of P sorption to sediments rich in iron oxides. Later in the summer, when sediments are more reduced, P is released and moves across the sediment-water interface. However, other mechanism of sediment P-release may also be involved and these will be examined later in this report.

Sediment fluxes of NO_2 + NO_3 were generally small compared to those of NH_4 and were mainly negative, that is directed from overlying water into sediments, thus representing at least a temporary loss of N from the water column. Median fluxes ranged from about 10 to - 50 µmol N m^{-2} hr^{-1}. The largest NO_2 + NO_3 fluxes were observed

during spring and very early summer and were directed into sediments. We have often seen this pattern (e.g., Stankelis et al 1999) and it seems to be, at least in part, driven by NO_3 concentration in overlying waters (Fig.6-3).

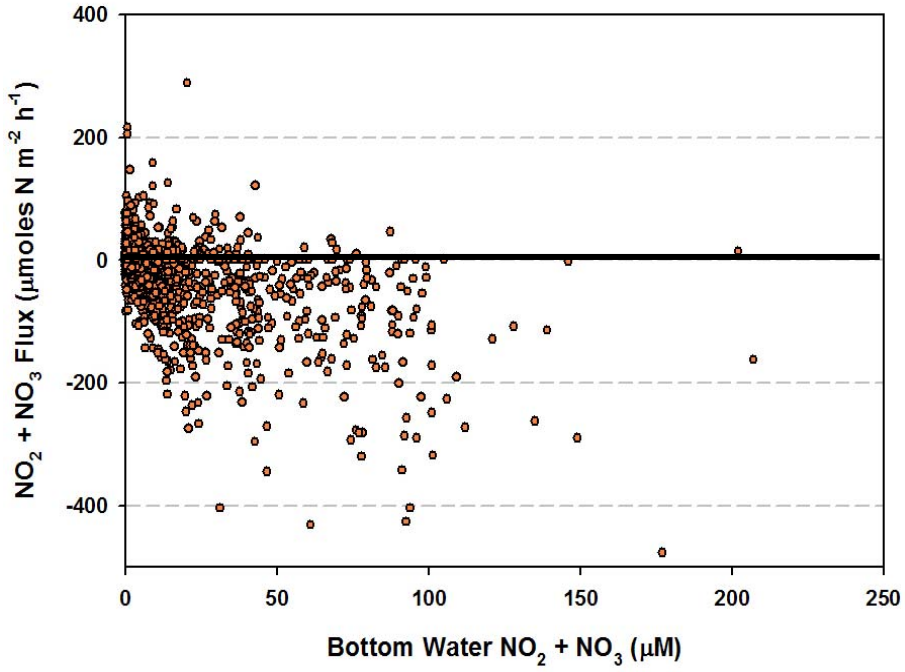

Figure 6-3*. Scatter plot of bottom water $NO_2 + NO_3$ concentration versus sediment $NO_2 + NO_3$ flux. All appropriate data in the data base were included in this analysis. Note that large negative fluxes were mainly associated with high nitrate concentrations.*

In both the mainstem Bay and tributary rivers water column nitrate concentrations reach maximum values during later-winter through spring (Chesapeake Bay Water Quality Monitoring Program 2007). The fate of this nitrogen is not quantitatively known but several authors (e.g., Boynton and Kemp 1985) have suggested that it is denitrified, representing a permanent loss of N from the system. Perhaps more interesting are the months of the year where some $NO_2 + NO_3$ emerges from sediments, mainly in the fall. We believe these positive N fluxes indicate that nitrification is active in surface sediments and is the source of this oxidized N. This is important as these positive fluxes indicate that sediments are sufficiently oxidized to support nitrification (production of nitrate from ammonium). Again, we do not know for sure but strongly suspect that most of this nitrate is denitrified in deeper, anoxic sediments. If the Bay restoration is successful to the point where large areas of Bay sediments remain oxidized through the warm months of the year then this nitrate could fuel considerable amounts of N loss through coupled nitrification-denitrification. If this were the case we would also predict smaller ammonium and phosphorus releases from sediments. In effect, this is the sequence of processes indicated in Figure 1-1 that represent an estuarine restoration trajectory. In another portion of this report we will discuss in more detail mechanisms influencing sediment N and P fluxes.

6-3. Influence of Temperature on Flux Patterns (Q_{10s})

One of the obvious master variables influencing many processes in aquatic ecosystems is water temperature. We have developed temperature versus sediment flux bar graphs to examine temperature influences for three of the sediment flux variables and also binned the data into salinity categories. In addition we also computed Q_{10} values for each sediment flux by salinity zone. (Figures 6-4 to 6-6). We did not compute Q_{10s} for NO_2+NO_3 flux because of the strong influence of water column NO_2+NO_3 concentration on this sediment flux.

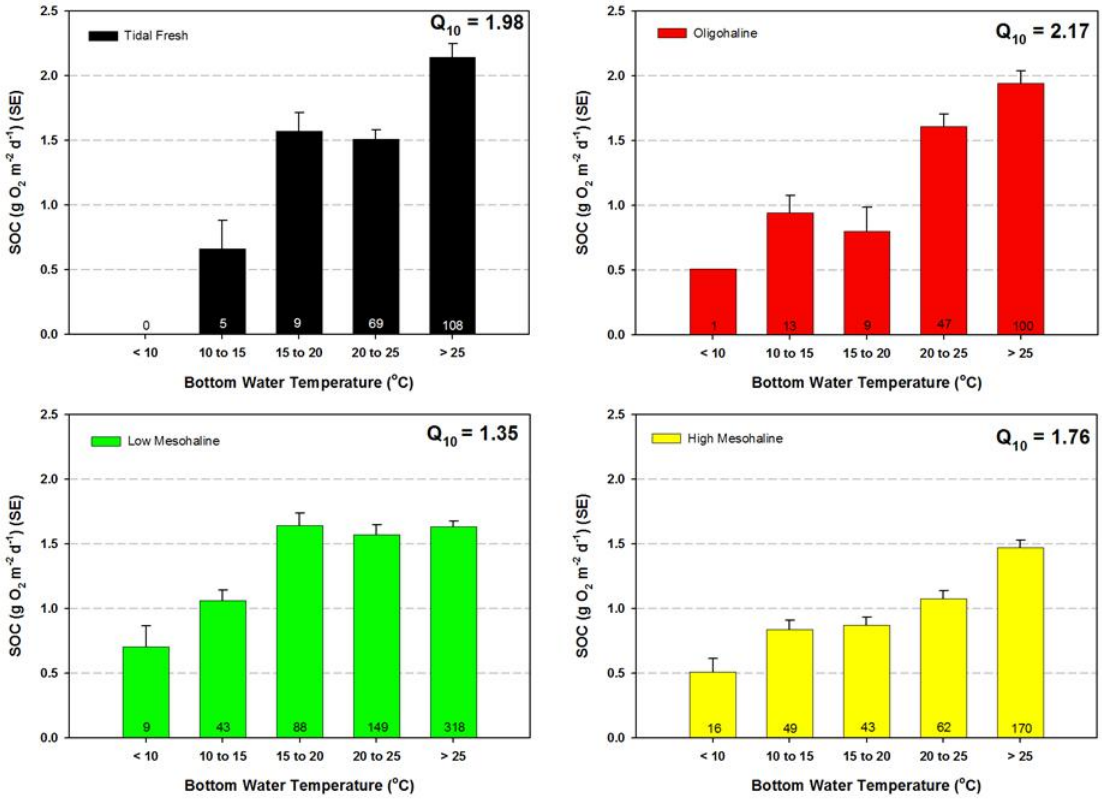

Figure 6-4. *Bar graphs (mean and standard error) of SOC by temperature categories. Data were separated into 4 salinity regions (0-1 = tidal fresh; 1-5 = oligohaline; 5 - 15 = low mesohaline; >15 = high mesohaline). Q_{10} values were calculated for each salinity zone. All Chesapeake Bay data were included.*

SOC rates in each salinity zone increased in response to temperature (Fig. 6-4). In some cases (oligohaine and high mesohaline) increases were progressive with temperature increases. In the tidal freshwater and low mesohaline sites temperature responses were less consistent. For example, SOC rates were essentially constant above 15 ºC at low mesohaline sites and were also constant between 15 and 25 ºC at the tidal freshwater sites. We suggest that substrate limitation (lack of labile organic matter) may be the cause but the quantitative basis for these variations in temperature responses is not really known. However, even with data binned by salinity zone there is great variability in environmental conditions among sites within a salinity zone (e.g., nutrient input rates,

algal deposition rates, sediment redox conditions) and, because of this, variation in rate responses to temperature would be expected. The fact that reasonably clear trends were evident indicates the importance of temperature-sediment flux influence. Q_{10} values computed for SOC at three of the four salinity zones were close to 2, a value often observed for rate processes and temperature. These simple values could be useful in modeling estuarine sediment dynamics.

Ammonium fluxes in each salinity zone also increased in response to temperature (Fig. 6-5). In most cases (oligohaine, low and high mesohaline) ammonium flux increases were progressive with temperature increases. In the tidal freshwater zone temperature responses were less consistent. For example, NH_4 fluxes were essentially the

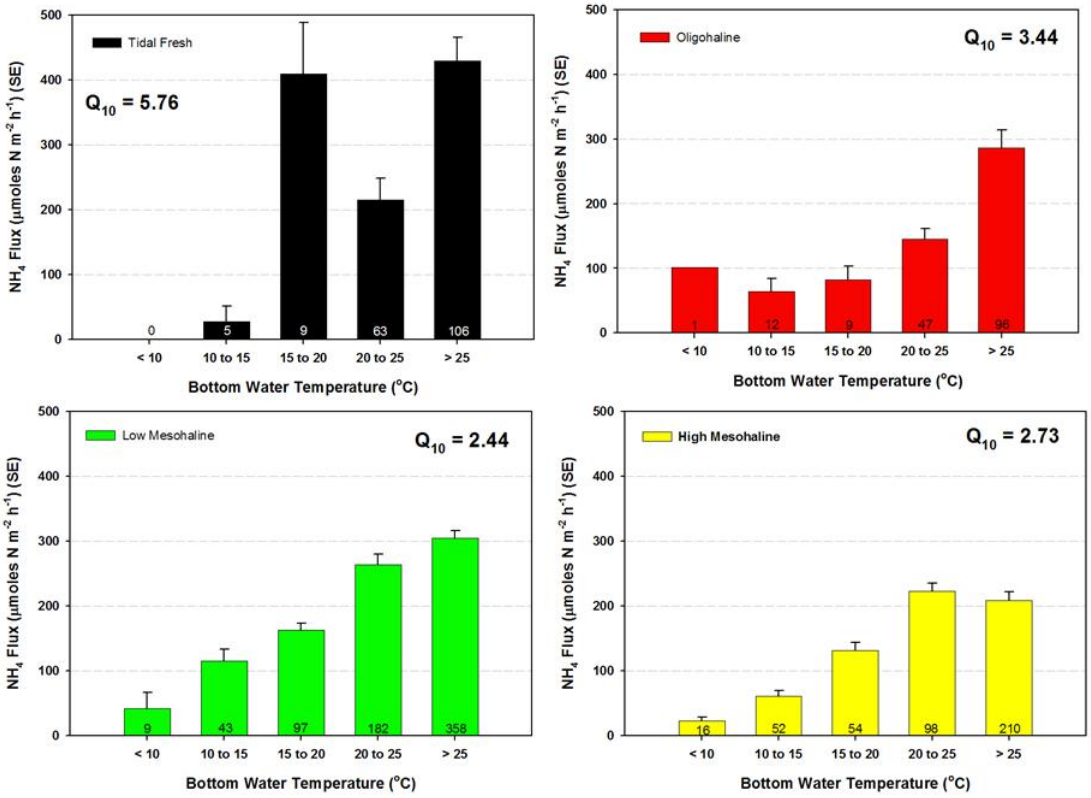

Figure 6-5. *Bar graphs (mean and standard error) of sediment NH_4 flux by temperature categories. Data were separated into 4 salinity regions (0-1 = tidal fresh; 1-5 = oligohaline; 5 - 15 = low mesohaline; >15 = high mesohaline). Q_{10} values were calculated for each salinity zone. All Chesapeake Bay data were included.*

same at 15 - 20 ºC and >25 ºC but less than half those at 20 - 25 ºC. The quantitative basis for these variations in temperature responses are also not known. However, even with data binned by salinity zone there is great variability in environmental conditions among sites within a salinity zone (e.g., nutrient input rates, algal deposition rates, sediment redox conditions) and, because of this, variation in rate responses to temperature would be expected. The fact that reasonably clear trends were evident indicates the importance of temperature-sediment flux influence. Q_{10} values computed for NH_4 flux at three of the four salinity zones ranged from 2.4 to about 3.4, similar in

magnitude to rates reported by Bailey (2005) based on sediment flux measurements made in estuarine systems other than Chesapeake Bay. The Q_{10} value for the tidal freshwater zone was very high and should be viewed with some skepticism. Again, these simple values relating a readily measured variable (temperature) to a sediment flux could be useful in modeling estuarine sediment dynamics.

Sediment phosphate fluxes in each salinity zone increased in response to temperature (Fig. 6-6). In most cases (oligohaine, low and high mesohaline) phosphate flux increases were progressive with temperature increases. In the tidal freshwater zone temperature responses were less consistent. For example, PO_4 fluxes increased gradually

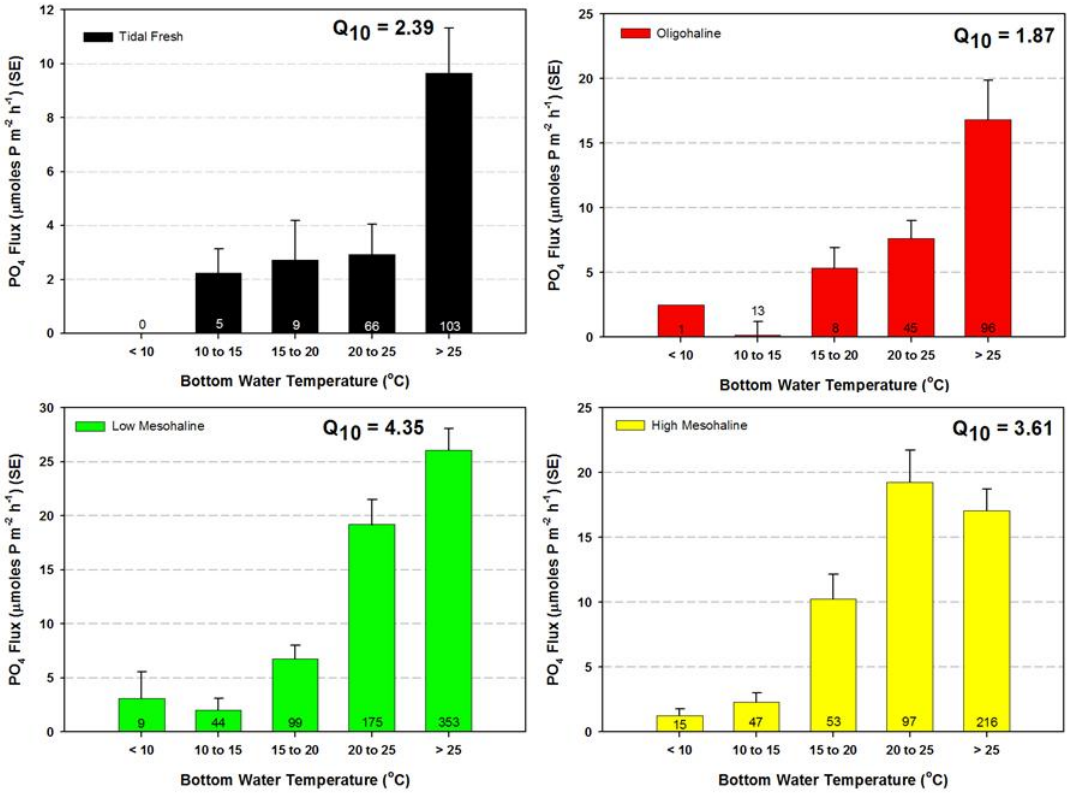

Figure 6-6. *Bar graphs (mean and standard error) of sediment PO_4 flux by temperature categories. Data were separated into 4 salinity regions (0-1 = tidal fresh; 1-5 = oligohaline; 5 - 15 = low mesohaline; >15 = high mesohaline). Q_{10} values were calculated for each salinity zone. All Chesapeake Bay data were included. The Q_{10} for the tidal fresh site excluded data at >25 °C and data from 10-15 °C at the oligohaline site.*

with temperature increases up to 25 °C and then increased by a factor of three at temperatures >25 °C. In this case the large increase in sediment P flux at high temperature may be related to sediment oxygen and redox conditions. Low sediment redox and low dissolved oxygen conditions, both of which promote sediment P flux, mainly occur at high temperatures in the Bay and tributary rivers. A portion of this large increase in P flux may be due to temperature but it is very likely that much of the increase is due to the release of P from iron oxides under very hypoxic and anoxic conditions.

However, even with data binned by salinity zone, there is great variability in environmental conditions among sites within a salinity zone (e.g., nutrient input rates, algal deposition rates, sediment redox conditions) and, because of this, variation in rate responses to temperature would be expected. The fact that reasonably clear trends were evident indicates the importance of temperature-sediment flux influence. Q_{10} values computed for PO_4 flux at three of the four salinity zones ranged from 1.9 to about 4.4, similar in magnitude to rates reported by Bailey (2005). Again, these simple values relating a readily measured variable (temperature) to a sediment flux could be useful in modeling estuarine sediment dynamics.

Bailey (2005) organized sediment flux data from 52 sites located in 48 different estuarine and coastal marine systems and we can use these data to compare both flux magnitude and flux responses to temperature (Fig. 6-7). In general, flux magnitude were similar or slightly lower than values measured in Chesapeake Bay and tributary rivers. In

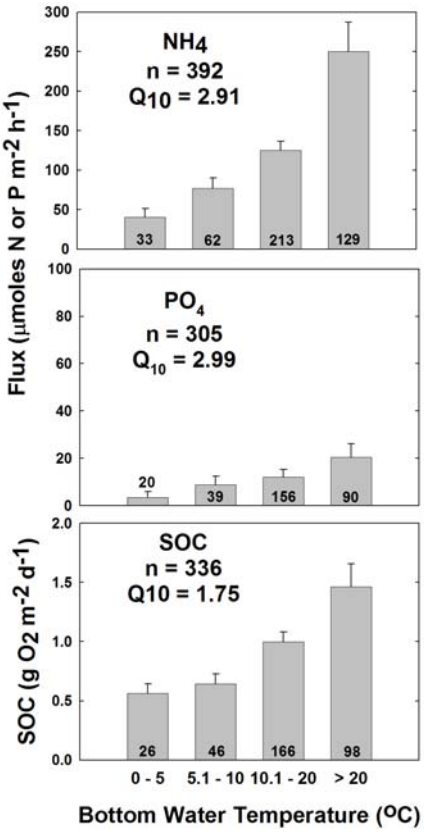

Figure 6-7. *Bar graphs (mean and standard error) of sediment NH_4 , PO_4, and SOC fluxes by temperature categories. Data were developed by Bailey (2005) from a literature review of sediment-water fluxes from estuaries other than Chesapeake Bay. Q_{10} values were calculated for each flux variable.*

addition, Q_{10} values for sediment SOC, NH_4 and PO_4 fluxes were quite similar to those observed in the Bay system. Again, there was great variability in environmental conditions at the sites summarized by Bailey (2005) yet there was strong and clear responses to temperature. This again suggests the importance of this variable on sediment flux dynamics.

While there is clear evidence of strong temperature influence on sediment fluxes, it would be a mistake to assume that other factors play minor roles in sediment flux regulation. Even the influence of temperature appears to be limited, at least in some locations in the Bay and tributary rivers. There are several sites in the Bay system where sediment fluxes were measured during most months of the year (February -November; in mesohaline mainstem Bay, mesohaline Potomac and Patuxent Rivers) thereby allowing for examination of temperature influence on flux through the full temperature cycle (Figs. 6-8 and 6-9). At all three sites there was a progressive increase in sediment flux with increasing temperature. However, ammonium flux declined rapidly at the mainstem Bay site (Fig. 6-8) after July despite the fact that water temperature was higher in August and September than it was in July. This decrease in flux between July and September was very large (~2X) and this pattern of strong decrease at equivalent temperature continued through October. Flux magnitude in November was close to that observed in May at similar temperatures. A similar temperature/sediment flux pattern was evident in both the Potomac and Patuxent mesohaline sites (Boynton and Kemp 2008; Fig. 6-9).

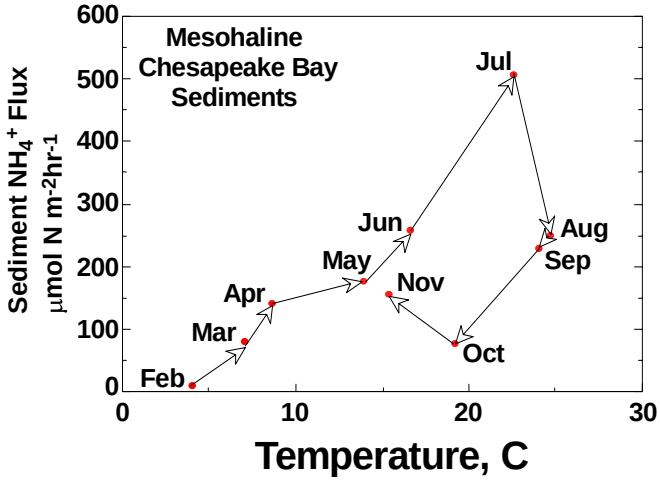

Figure 6-8. *Progressive scatter plot of monthly temperature versus sediment NH4 flux based on data collected in the mesohaline portion of mainstem Chesapeake Bay.*

This decoupling of the generally strong temperature - flux relationship may best be explained by organic matter limitation. In short, we suggest that during the late winter and early spring labile organic matter from the spring diatom bloom is deposited to the sediment surface and when bloom deposition is completed sediments are as "organic matter loaded" as they will be for the remainder of the year. At that time (February-April) bottom water temperature is low enough to restrict remineralization to small rates. As temperature increases, so does sediment flux. However, Boynton et al (1991) have shown that during the summer, deposition of labile organic matter to sediments is lower and water column respiration of depositing material higher (Smith 2000). Thus, the supply rate of organic matter from late spring through late summer is not sufficient to support remineralization rates at high temperatures. In the previously presented flux - temperature relations by salinity zone there were suggestions of some limitation other than temperature at both low and high mesohaline sites, consistent with the organic

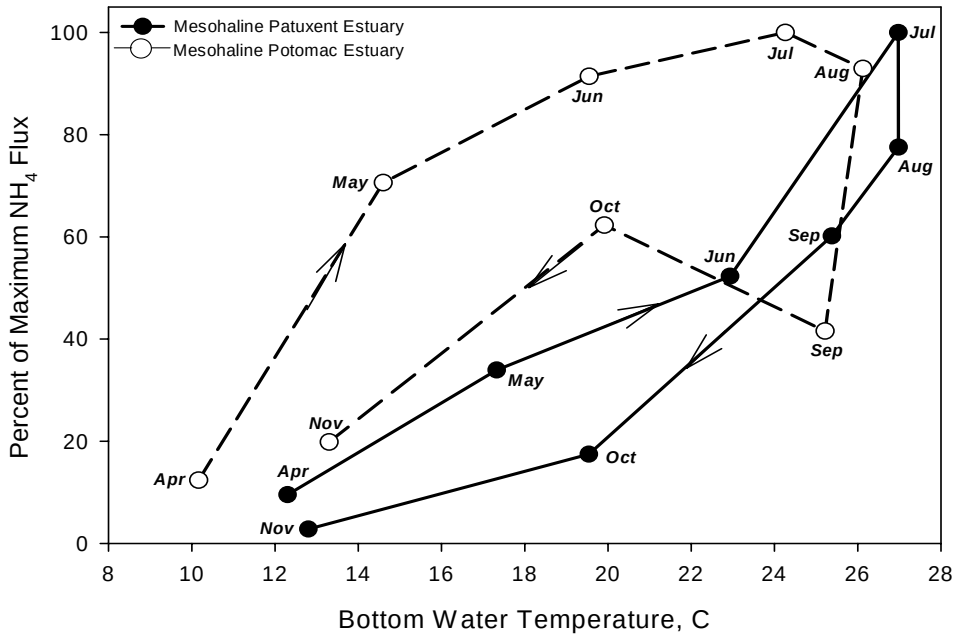

Figure 6-9. *Progressive scatter plots of bottom water temperature versus station specific percent of annual maximum sediment NH_4 flux at two sites in Chesapeake Bay tributaries (mesohaline Potomac and Patuxent River estuaries). Figure was adapted from Boynton and Kemp (2008).*

matter supply argument. This finding, if general, has an important implication for both water quality modelers and for those managing Bay restoration. This argument suggests that there is little labile organic matter or nutrient memory in the Bay system. Sediments in these shallow systems are the only component where there is even the potential for inter-annual nutrient, or any other material, storage. Boynton et al (2008) has shown that most of the N and P in the Patuxent River estuary is in the top few centimeters of the sediment column. Thus, water quality conditions are largely determined by conditions of inputs occurring on an annual basis. If, for example, nutrient inputs decline we would expect water quality conditions to improve rapidly. Similarly, water quality modelers should not assume that there is a large reserve of nutrients in sediments that are also biologically active. While most of the N and P in these systems is in sediments, most of it does not appear to be very available for biological processes.

6-4. Regulation of Sediment-Water Fluxes

There are many factors, in addition to temperature, that play important roles in regulating sediment biogeochemical processes and associated sediment fluxes. There is a substantial literature concerning this topic, extending back several decades. The list of potential influencing factors, in addition to temperature, include activities of infaunal communities, redox conditions near the sediment-water interface, solute concentrations in overlying water, and rates of organic matter supply. Effects of infauna can be both direct (i.e., excretion) and indirect (i.e., burrowing, pumping, and stimulation of microbial communities). For example, Flint and Kamykowski (1984), Hammond et al (1985), Kanneworff and Christensen (1986), Banta et al (1995) and Webb and Eyre (2004)

reported a variety of macrofaunal influences on sediment-water exchange rates and other processes. Others have reported on the influence of redox and water quality conditions on sediment processes (e.g., Sundby et al 1992). The challenge of quantitative modeling of sediment-water processes and associated interactions was captured in a recent book by DiToro (2001).

Previous studies have concluded that, ultimately, organic matter supply rate to sediments was the overarching factor regulating sediment biogeochemistry and nutrient flux across the sediment-water interface. For example, comparative analysis among diverse estuarine systems indicates that benthic respiration rates are highly correlated with organic matter production rates (Nixon 1981). The relationship appeared to be linear across a very large range of primary production rates (~ 75 to 1400 g C m^{-2} y^{-1}), including data collected from several locations from Chesapeake Bay (Kemp and Boynton 1992). In northern European waters, rates of sediment respiration and ammonium and phosphorus fluxes tend to respond rapidly to deposition of spring and autumn algal blooms (Graf et al 1982; Jensen et al 1990). Although temperature appears to affect response time, similar relationships have been reported for sediment anaerobic respiration in North American systems (Sampou and Oviatt 1991; Marvin-DiPasquale et al 2003).

Interacting effects of organic matter supply and temperature can be illustrated with examples from Chesapeake Bay sediments. In the first case (Cowan and Boynton 1996), sediment chlorophyll-a concentration (as an index of recent organic deposition) was related to sediment-water NH_4 fluxes measured during three years at three stations along the estuarine salinity gradient (Fig. 6-10). Even with the inclusion of data collected

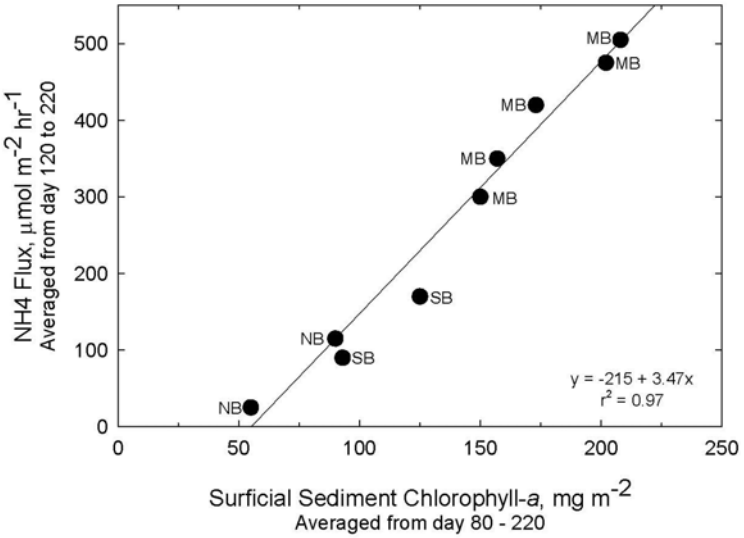

Figure 6-10. *Scatter plot of surficial sediment chlorophyll-a versus sediment NH_4 flux. Surficial sediment chlorophyll-a data (top 1 cm of sediments) were averaged for each site and year between days 80 and 220; sediment flux data were averaged for the period between days 120 and 220 for each year. These data were collected by Cowan and Boynton (1996). Abbreviations NB, MB and SB refer to sampling sites in the north, mid and south portions of mainstem Chesapeake Bay.*

in different years the strength of this relationship is striking. These stations varied

substantially in terms of mean depth, O_2 conditions, sediment type, and macrofaunal characteristics; the strength of the observed relationship, therefore, emphasizes the overall importance of organic matter supply. A second point of great importance in this analysis is the lag time used in relating organic matter availability and sediment flux. Specifically, sediment chlorophyll-a concentrations were averaged from just prior to spring bloom deposition through the summer period, while NH_4 fluxes were averaged from mid-spring through summer. Biogeochemical processes in this system, which has a large annual temperature range (0 to 33 ºC), are apparently not adapted to cold water (Sampou and Kemp 1994). We argue that sediment respiration and nutrient remineralization respond to spring bloom deposition and labile organic matter accumulation primarily after temperature increases beyond 15 ºC (Cowan and Boynton 1996). Thus, there is a period of organic matter loading to sediments followed by a period of NH_4 release. Other investigators have found a more immediate response to temperature (e.g., Banta et al 1995). However, the importance of organic matter supply rate is clearly evident in these results.

We binned summer ammonium flux data by salinity regimes and plotted these as a function of sediment total chlorophyll-a mass (again, an index of labile organic matter; Fig. 6-11). In all salinity regimes there was a general increase in ammonium flux with increasing sediment chlorophyll-a mass but there was also a very large degree of scatter. Part of this unexplained variance is to be expected when a large number of observations are examined. However, we believe these relationships would be considerably stronger if we had a measure of spring sediment chlorophyll-a mass, as was the case in the work of

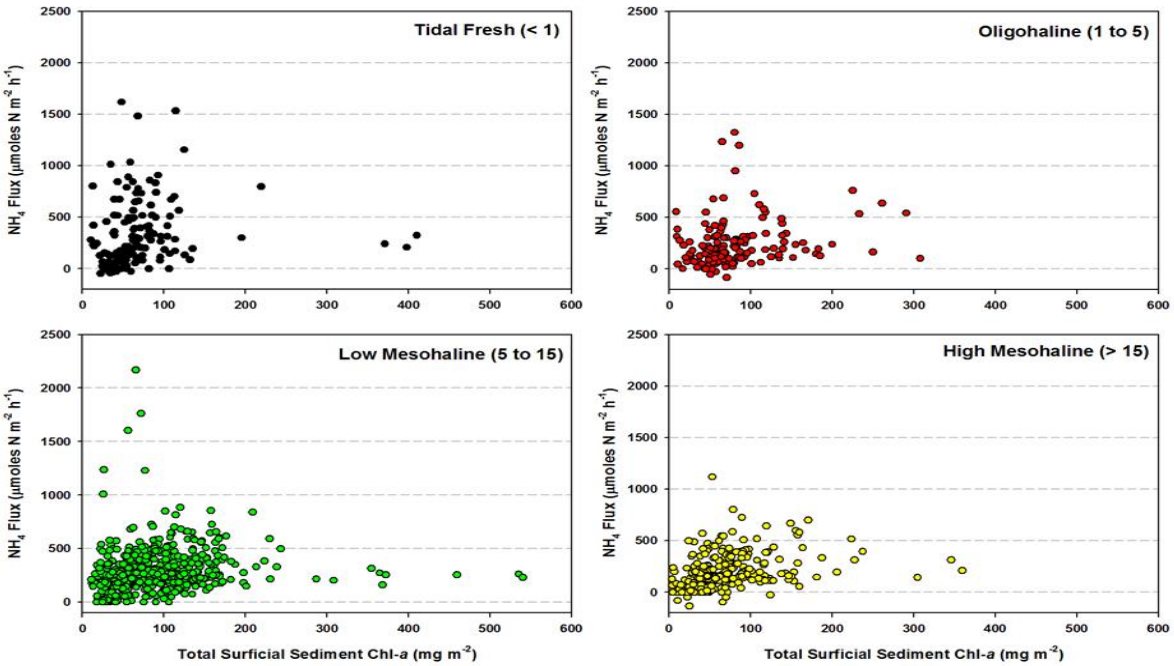

Figure 6-11. *Scatter plots of sediment NH4 flux as a function of total sediment chlorophyll-a mass (to depth of 1 cm). Data were sorted by salinity zone. These plots contain data from all sites in the database.* collected during June, July and August.

Cowan and Boynton (1996) and Stankelis et al (1999). Unfortunately, in most sediment

flux measurement programs there were no sediment measurements made prior to the usual June-August measurements.

The second example is from the Patuxent River, where multiple NH_4 flux measurements were made during three summer periods, all within the mesohaline region of the estuary (Stankelis et al 1999). Water column and sediment characteristics were also measured at flux site locations and a reasonably simple regression model was developed in which sediment chlorophyll-a, as an index of labile organic matter supply,

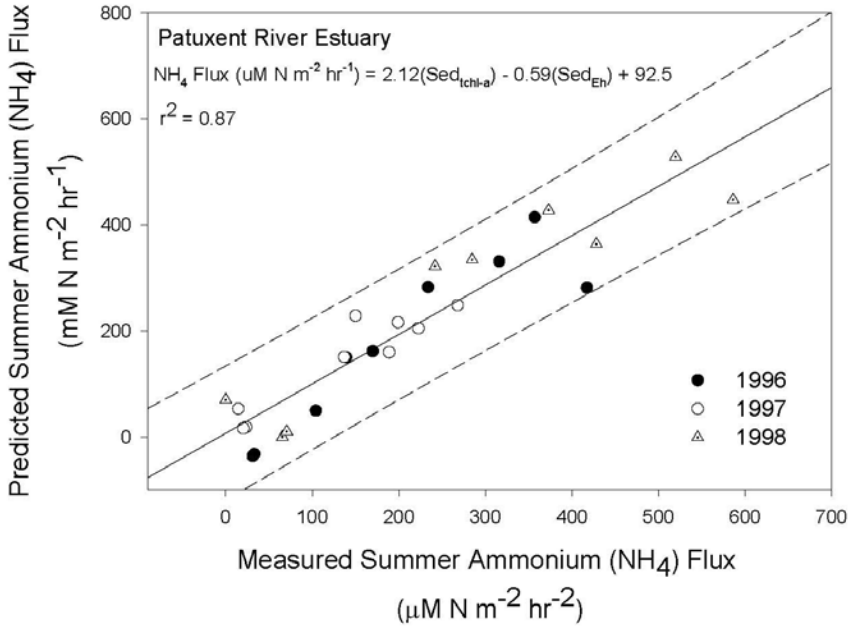

***Figure 6-12**. Actual (measured) versus predicted summer (June-August) sediment NH_4 fluxes measured at stations in the mesohaline region of the Patuxent River estuary. Plot includes data collected during three successive summer periods. Sampling sites spanned a range of environmental conditions including sediment type (sand to mud), depth (3 to 18 m), and sediment redox conditions (oxidized to very reduced). A very similar pattern emerged for sediment PO4 fluxes with sediment chlorophyll-a and deep water PO4 concentration (probably a co-correlate of sediment redox conditions) being the independent variables. These analyses were developed by Stankelis et al 1999).*

again played an important part (Fig. 6-12). An additional twist in this analysis was the apparent role played by sediment redox conditions. The model indicated that as sediment redox conditions became more positive, less NH_4 was released. This is consistent with the idea that sediment N is more likely to be nitrified (and then denitrified) when sediments are oxidized (Kemp et al 1990; Rysgaard-Petersen et al 1994).

6-5. "Take-Home" Summary

- This analysis of sediment flux in Chesapeake Bay was based on approximately 1500 measurements collected from about 280 different sites
- The majority of measurements (72%) were collected during the summer months (June - August) when sediment processes are most active; about 12% of

measurements were made during spring and the same percentage during fall. Only 5% of all measurements were made during winter.

- There were very strong seasonal patterns of flux for SOC, NH_4, PO_4 and NO_2 + NO_3. SOC and NO_2 + NO_3 fluxes peaked during late spring - early summer and NH_4 and PO_4 fluxes peaked during summer. Winter rates were always low for all sediment fluxes and low enough to have little influence on water quality conditions.
- There is clear evidence of strong temperature effects on sediment fluxes. Calculated Q_{10} values were generally in the range of 1.5 to 3.5 with a few higher values. These values compared well with Q_{10s} computed for other estuarine and coastal marine environments.
- However, it also appears that in some portions of the Bay and tributary rivers the temperature - flux relationship fails later in summer and fall. Late summer and fall sediment fluxes are often lower than those observed in late spring and early summer at similar temperatures.
- Analyses of sediment flux time-series data in several areas of the Bay indicate that the supply rate of labile organic matter to sediments is a master variable constraining the magnitude of summer and early fall fluxes. Other environmental conditions (e.g., temperature, sediment redox conditions) modify the timing and other characteristic of sediment flux but labile organic matter supply rate ultimately constrains these processes.
- The last two conclusions suggest that there is little nutrient memory in the Bay. Water quality modelers should not take the liberty of using nutrients stored in sediments to influence water quality conditions much beyond a single year. Our analyses suggest that the "sediment flux clock" is set each year with the deposition to the sediment surface of spring bloom organic matter (and supplemented to a lesser degree by summer bloom deposition) with little influence from deposition events in previous years.

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Chapter 7

Role of Depth and Water Column Respiration on the Relative Importance of SOC

7-1. Background

One of the central issues facing Chesapeake Bay management and restoration programs concerns the existence and expansion of hypoxic and anoxic zones in estuarine waters throughout the Bay system (Hagy et al 2004). Such hypoxic/anoxic zones have become common features of estuarine and coastal waters throughout the world and well over 100 such zones have been identified. Essentially these oxygen depleted areas occur when rates of oxygen depletion, due mainly to biological and chemical oxygen demand, exceed rates of oxygen supply from physical (i.e., advection, dispersion, and air-sea DO exchange) and biological (i.e., net photosynthesis) processes.

In an earlier evaluation of the relative importance of physical and biological processes in creating and maintaining hypoxic conditions in the mesohaline region of Chesapeake Bay, Kemp et al (1992) found the following: 1) sediment oxygen consumption was a dominant oxygen sink during spring and then again in late summer when reduced compounds (reduced S compounds from anaerobic respiration in sediments) were oxidized, 2) in water columns deeper than 5 meters planktonic respiration was more important than benthic respiration, 3) there were strong correlations between biological and physical oxygen processes wherein biological processes generated DO gradients that influenced rates of physical transport and 4) relatively large reductions in biological respiration rates would lead to smaller decreases in hypoxic volumes because of this coupling between physics and biology. Hagy (2000) also examined oxygen sources to deeper waters of the mainstem bay and found that deep water advection (landward) of oxygen dominated in the lower Bay while vertical oxygen transport was more important in the mid-Bay region of the hypoxic zone. One of the main issues in this synthesis is to better understand the relative role of sediment processes in the initiation and maintenance of hypoxia in the Bay region. This being the case we need to be able to understand the relative importance of SOC versus water column respiration.

7-2. Water Column Respiration Rate Measurements

Despite the observation that water column respiration is a key process in the formation and maintenance of hypoxic conditions, water column respiration has never been measured in the Chesapeake Bay monitoring program. Thus we are left with a major process that has been less well documented, especially in a time-series fashion. However, Smith (2000) made about 250 measurements of euphotic zone primary production (P) and water column respiration (R) along the axis of the mainstem Bay. Respiration rates for the euphotic zone (5-9 m depth) ranged from near-zero to 11 g O_2 m^{-2} day^{-1}, with most rates in the range of 1 to 5 g O_2 m^{-2} day^{-1}. In addition, Smith (2000) found strong seasonal changes in rates (generally following temperature) and that very small heterotrophs constituted the main water column consumers of organic matter and oxygen. These rates are generally larger than SOC measurements for mesohaline portions

of the Bay at comparable temperatures and indicate the importance of water column respiration in the Bay hypoxia story.

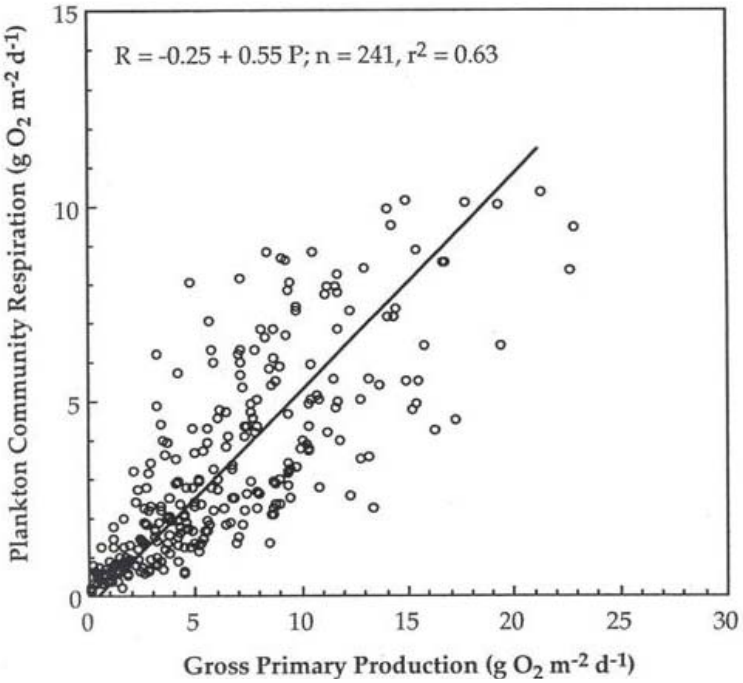

Figure 7-1. *A scatter plot of all euphotic zone gross primary production versus all euphotic zone respiration rates measured by Smith (2000) along the mainstem axis of Chesapeake Bay. Note the range in depth integrated respiration rates (y-axis).*

Partly in response to the paucity of water column respiration measurements and because of the importance of this process we began making water column respiration measurements during the MDE-supported TMDL sediment-water oxygen and nutrient exchange program. During a portion of this program surface water respiration rate measurements were conducted using the oxygen-based dark bottle approach with 24 hour incubation at ambient water temperature. Such measurements were made at each station and sampling date in the following Bay tributary systems: Anacostia, Potomac, all small western shore tributaries, Corsica and the Maryland Coastal Bays. There were a total of 182 surface water respiration rate measurements made and all of these are included in the database.

Respiration rates from all sites ranged from near zero to almost 5 g O_2 m^{-3} day^{-1}; median rates between May and October ranged between 1.5 and 2 g O_2 m^{-3} day^{-1} (Fig. 7-2a). These rates have been expressed on a volumetric basis; to be directly comparable to those reported by Smith for the mainstem Bay our rates need to be multiplied by water column depth. Monthly rates collected at multiple stations in tributary rivers are shown in Figure 7-2b. Here rates varied from about 0.5 g O_2 m^{-3} day^{-1} to 5 g O_2 m^{-3} day^{-1}. There was, even for the abbreviated portion of the year which measurements were available, an indication of temperature influence with highest rates in August and lower rates in May and October. Respiration rates at all sites but the Corsica River were similar

in magnitude; average monthly rates ranged from about 0.5 to about 2 g O_2 m^{-3} day^{-1}. However, rates in the Corsica were very large (about 5 g O_2 m^{-3} day^{-1} in August), and close to many vertically integrated rates reported by Smith (2000). The extreme rates in the Corsica likely resulted from the extreme algal biomass (chlorophyll-a concentrations > 200 µg l^{-1}) supported by large diffuse source nutrient loads often observed in this tributary river.

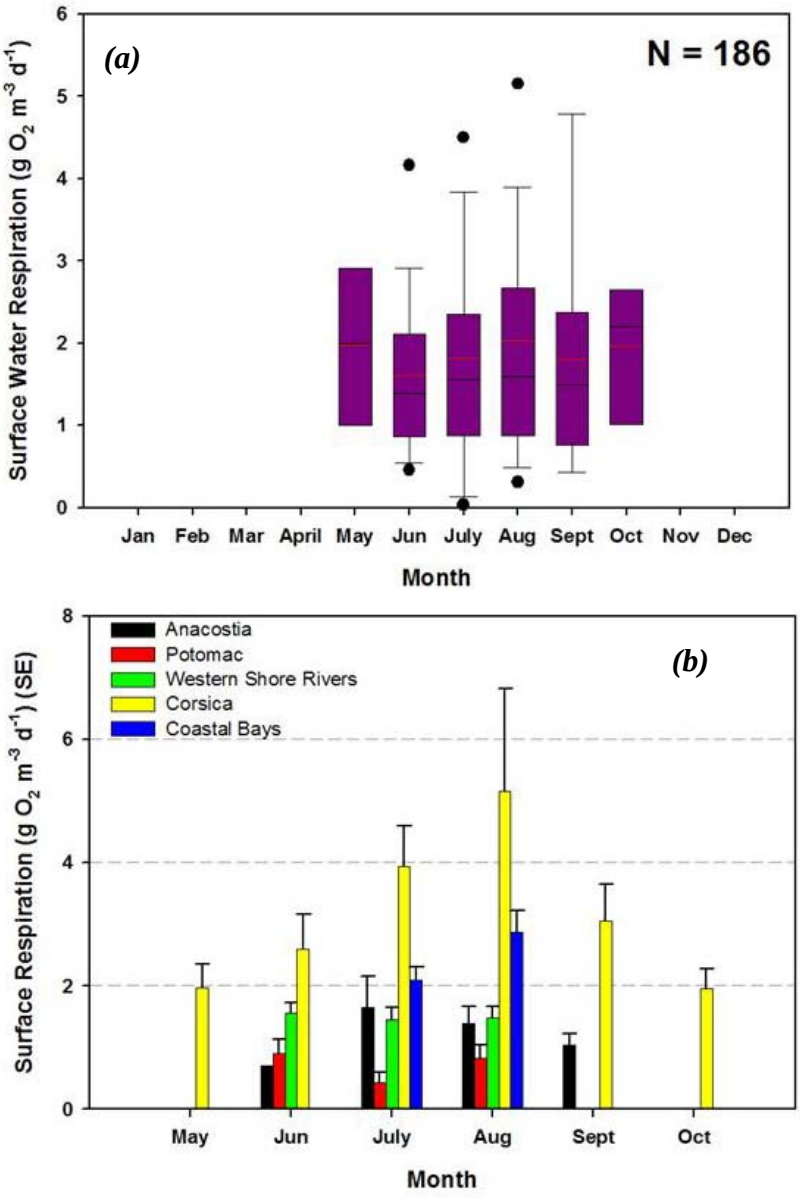

Figure 7-2. *Box and whisker plots of surface water respiration rates by month for all sites combined (a) and average (plus or minus one standard error) monthly rates for tributaries where respiration measurements were completed (b). All rates are volumetric.*

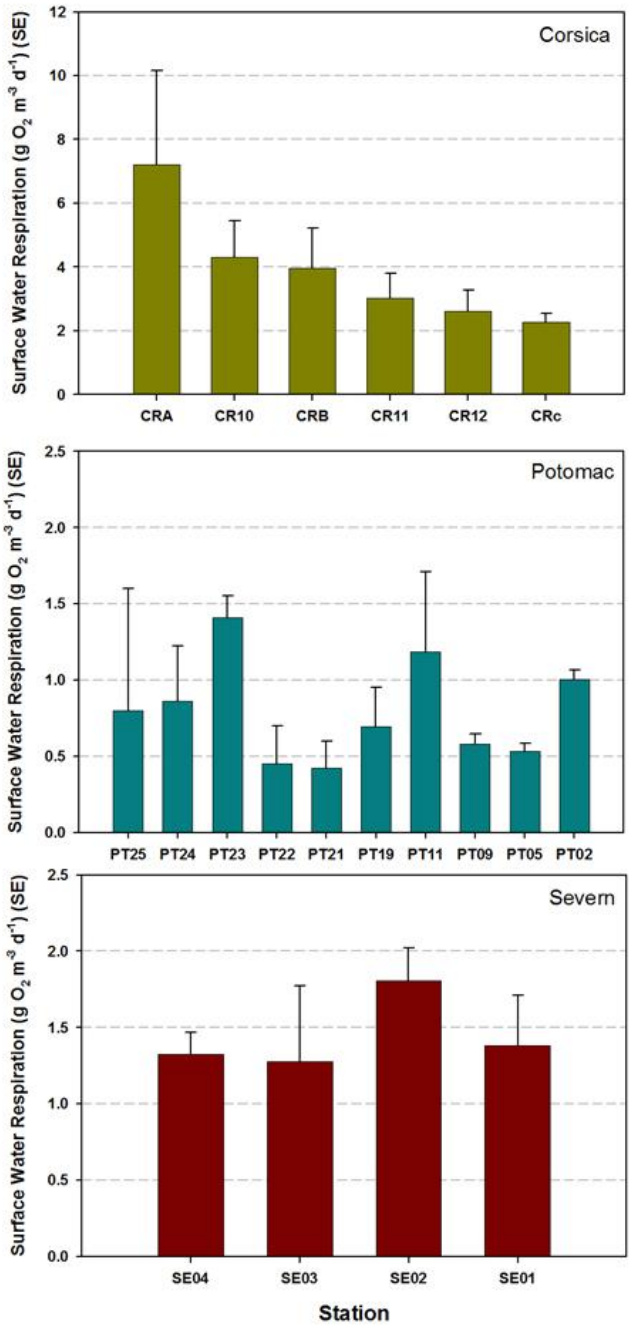

Figure 7-3. *Bar graphs (mean and one standard error) of volumetric respiration rates for three Chesapeake Bay tributary rivers during June-August (see Fig. 3-1 and Table 3-4 for locations). Stations (x-axis) are arranged from upstream to downstream (left to right). Note the y-axis scale change in the upper panel.*

Water column respiration rates measured along estuarine salinity gradients are also available for a few of the tributary rivers (Fig. 7-3). Respiration rates along the axis of the Corsica River estuary were very large and decreased from the head of the estuary, where algal stocks were especially large, to the junction with the Chester River estuary. Rates of 7 g O_2 m^{-3} day^{-1} were among the highest measured during our TMDL program. Respiration rates along the main axis of the Potomac River estuary, also for a summer period, were much lower than those observed in the very eutrophic Corsica River estuary

and did not exhibit clear spatial patterns. Respiration rates in the Severn River estuary, a small flooded river valley estuary in the mid-Bay region, exhibited rates that were uniformly higher than those in the Potomac but still only about half those observed in the Corsica. With this small and seasonally constricted set of water column respiration rate data it is difficult to discern many reliable patterns. However, it is safe to assert that at most locations in the Bay and tributary rivers water column respiration is a significant factor in DO budgets, especially during warm seasons of the year. As we will show later in this Chapter, in deeper portions of the Bay water column respiration is the dominant biological term in oxygen budgets.

It would have been very useful to have time-series of water column respiration measurements available to examine for temporal trends and for possible relationships to other environmental variables, some of which have been modified by management actions (e.g., nutrient load reductions in the Potomac, Back and Patuxent rivers). In addition, it would have been useful to examine across eutrophication gradients the relative importance of water column versus sediment oxygen consumption rates. However, water column respiration data are simply not available to do this. Since water column respiration is a significant oxygen sink, we recommend that more attention be focused on making routine, high quality respiration measurements as part of monitoring program activities.

7-3. Depth and SOC and SOC vs Water Column Respiration Relationships

Averaged over annual time-scales, the relative importance of benthic and planktonic water column DO consumption should depend largely on mean depth of the water column, as first suggested by Hargrave (1973). Indeed, previous studies have shown that SOC is inversely proportional to water column depth across large (10 m to 10 km**)** depth gradients (Harrison 1980, Suess 1980). However, Kemp et al (1992) found a similar pattern (Fig. 7-4a) for estuaries and coastal sheIf systems, which range over a much smaller depth gradient (1 to 60 m). This implies that the amount of euphotic zone organic matter which sinks to the sediment surface to support SOC decreases as longer water columns increase the transit time (and attendant opportunity for consumption by heterotrophic plankton) for sinking substrates. These authors also considered sites for which contemporaneous summer and/or spring measurements of both benthic and planktonic respiration rates were available. The strength of this relation (Fig. 7-4b) is surprising given the fact that seasonal (rather than annual) mean rates are compared, and it suggests that the pattern is robust. A similar exponential declining relation with depth is found when SOC is presented as a fraction of total community respiration. Here, plankton respiration is integrated over the entire water column rather than just the lower layer so as to include both stratified and non-stratified systems in the comparison. Thus**,** for example, data from the Kemp et al (1992) study (Fig. 7b) suggest that SOC represents a smaller fraction (10 to 20 %) of community respiration rather than the range (20 to 40 %) found for bottom layer respiration only (Fig. 7-4a). From this relation, we would expect SOC to dominate community respiration only in water columns (or bottom water layers) of 5 m height or less. This is of particular significance in Chesapeake Bay and tributary estuaries because of the shallow water depths characteristic of these systems.

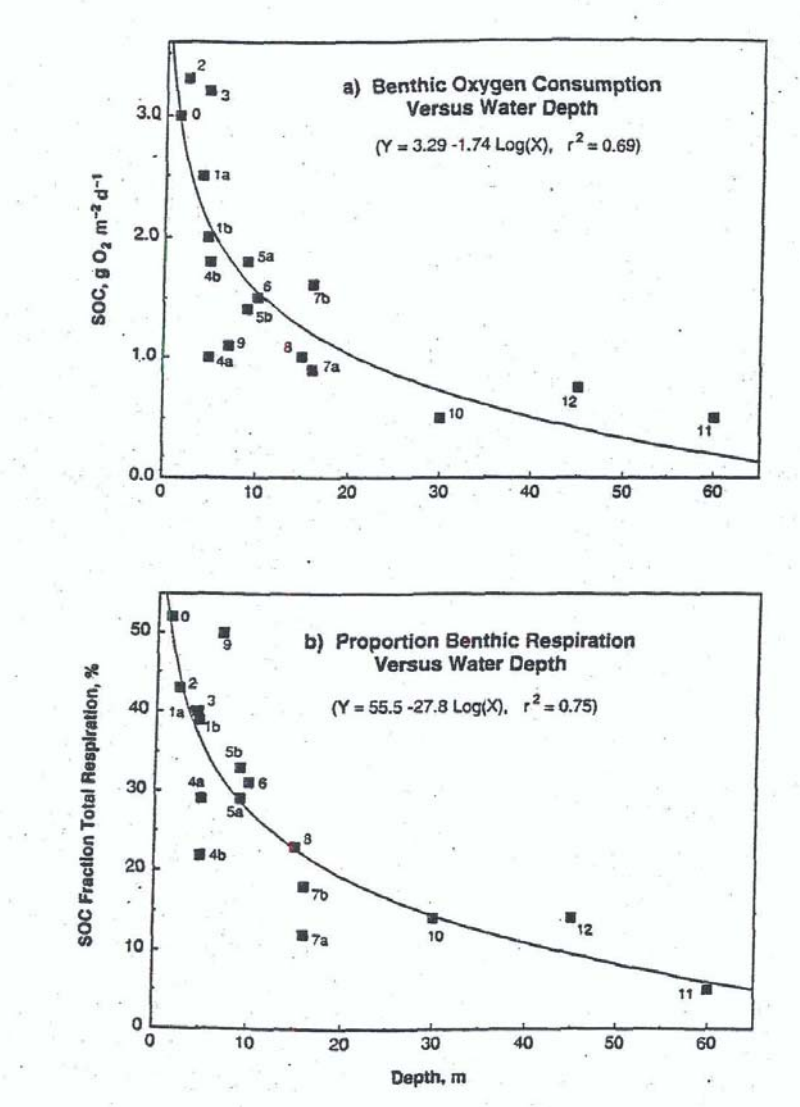

Figure 7.4. *Summary of mean spring and summer measurements of (a) sediment DO consumption (SOC) as a function of depth and (b) SOC as a percent of total respiration plotted against total water column depth. Numbers beside points refer to data sources which are listed in Kemp et al (1992).*

We have organized Chesapeake Bay station depth, SOC and total water column respiration data to see if the depth related patterns discussed above emerge for a data set wherein the range of depths is even more limited (range = 1-42 m; median depth = 6 m).

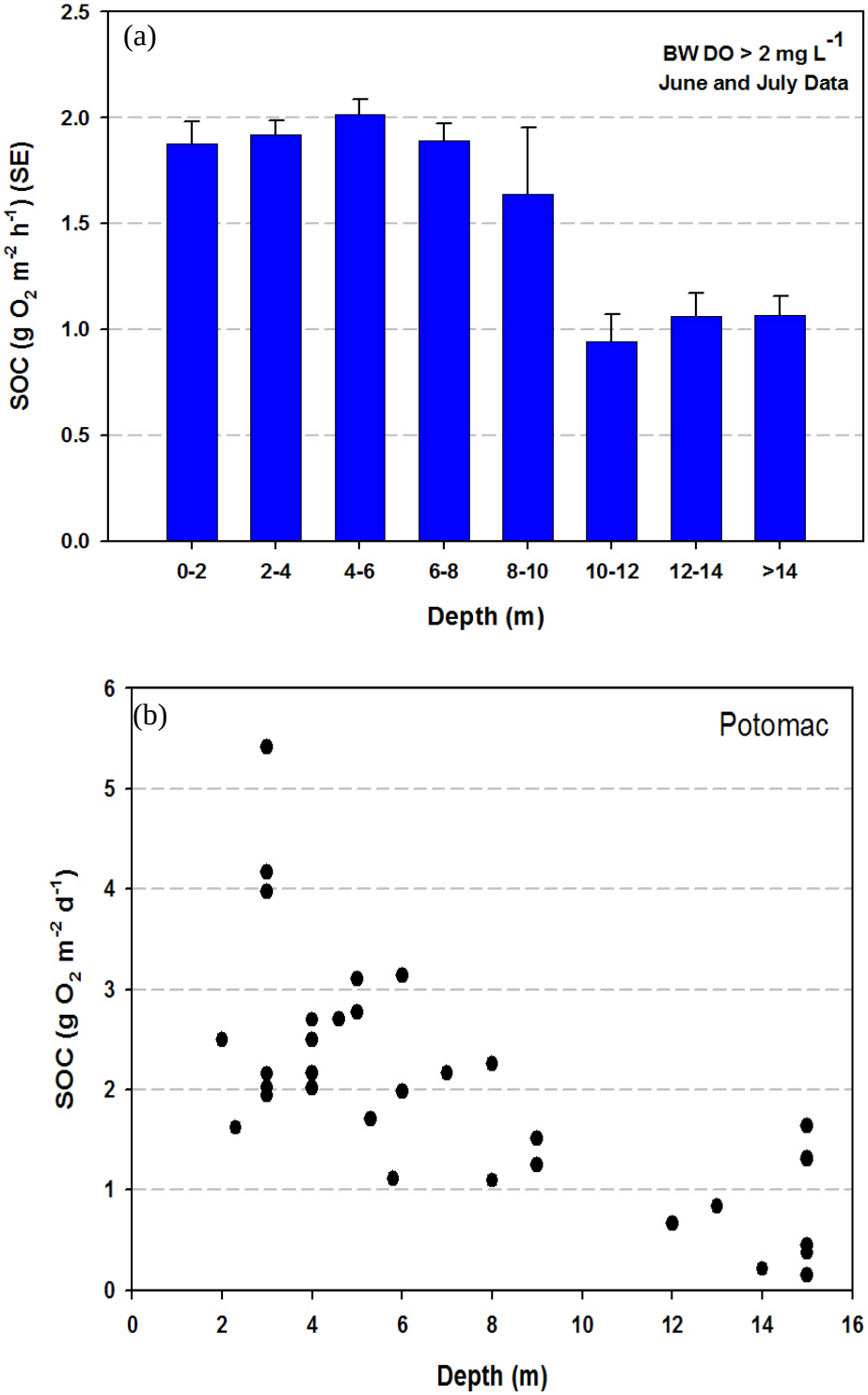

Figure 7-5. *Relationships between SOC and water column depth for (a) flux data set for the months of June and July and sites where bottom water DO >2.0 mg l^{-1} and (b) for all SOC data from the Potomac River estuary where bottom water DO > 2.0 mg l^{-1}. SOC data were excluded in cases where bottom water DO < 2.0 mg l^{-1} because low DO limits SOC rates.*

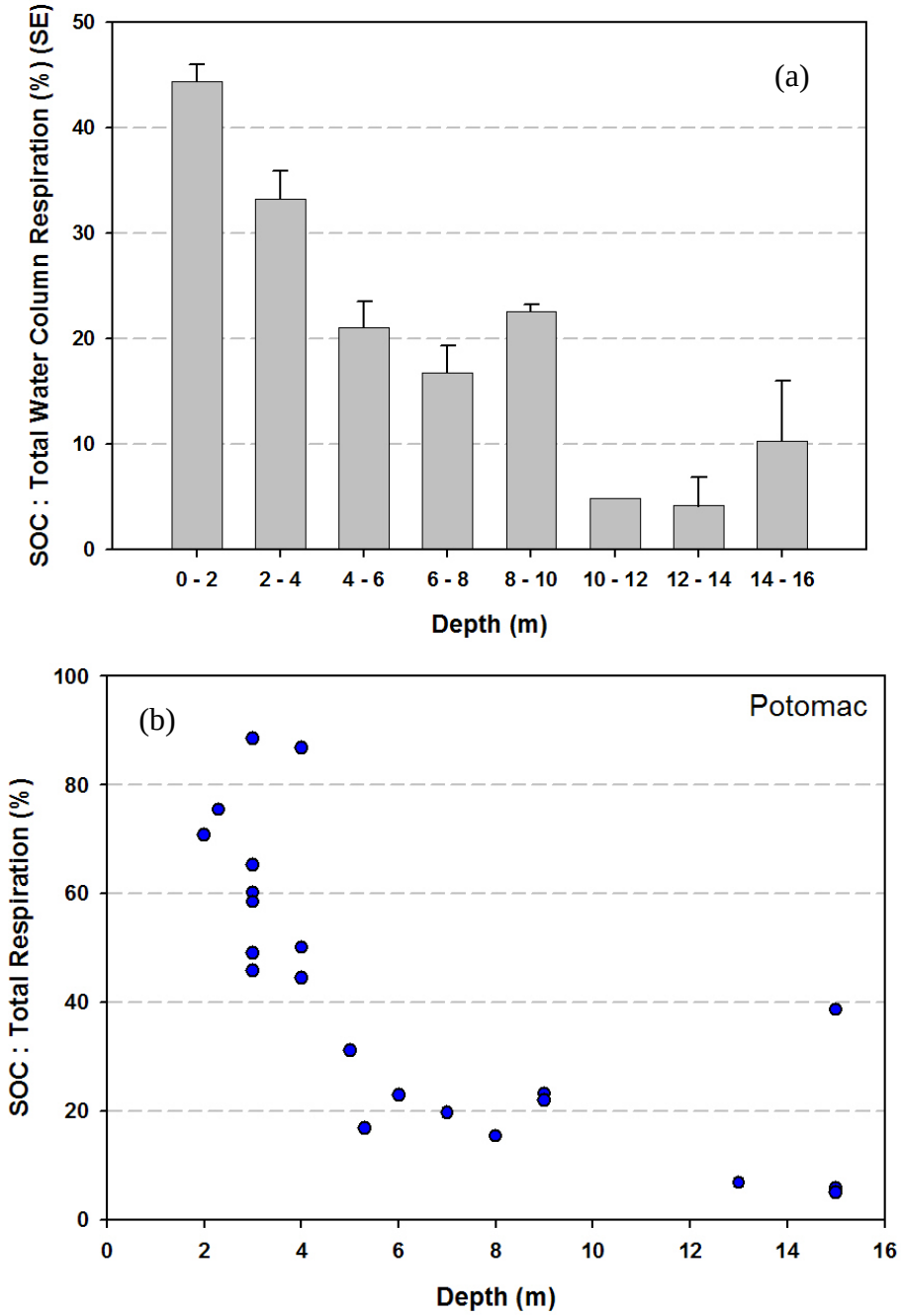

Figure 7-6. *Relationships between station depth and the ratio of SOC :total water column plus SOC for (a) the full Bay data set (June and July data at sites where bottom water DO > 2 mg l^{-1} and (b) for data collected along the axis of the Potomac River estuary (June-August data at sites where bottom water DO > 2 mg l^{-1}*

SOC data arranged by depth interval for the full Bay data set (June-July data at sites where bottom water DO > 2.0 mg l^{-1}) exhibited a similar pattern to those reported by Kemp et al (1992). SOC rates increased slightly from 2 to 6 m depths and then decreased by about a factor of two at the deeper depths (Z > 14 m). The reason for the slight depression of rates at shallow sites is likely to be related to one of two factors or some combination of those factors. First, the sediment surface at very shallow sites (< 2 m) is subjected to wind-induced wave action on a far more regular basis than sediments at deeper sites. As a result of this, such sediments tend to be better sorted with sands being the dominant grain size and organic matter content depleted. Thus, SOD rates at these sites might be lower because of a limited supply of labile organic detritus to support aerobic metabolism. Second, it is possible that at some shallow sites enough light penetrated to the bottom so that there is some autotrophic production rather than just heterotrophic activity. Since all the sediment cores used in these measurements were incubated in the dark it is unlikely that SOC rates were lower because of DO production from heterotrophs. However, there may be some interaction with autrotrophs that leads to lower rates of SOC. In any case, the depth-related differences in SOC at depths from 1 to 6 m were small. However, depth related decreases in SOC beyond 6 m were substantial (~2x) and similar in pattern to that reported by Kemp et al (1992) except in our data set the depth range was even smaller. We have been able to exclude the effect of low bottom water DO concentrations on this relationship by excluding sites were low bottom water DO concentrations limited SOC (bottom water DO < 2.0 mg l^{-1}). We also examined SOC versus depth using the Potomac River estuary data set because there were numerous sites where sediment flux measurements were made and because there was a substantial range in depths encountered. With substantial scatter, the same pattern emerged wherein highest SOC rates occurred at shallow depths (~3 m) and decreased rapidly with further increases in depth. While we are finding substantial decreases if SOC with depth, the rates reported even at depths >15 m are still of ecological importance in that they have impact in developing hypoxic and anoxic conditions. In both the full data set and the Potomac data set deep water rates were about 1 g O_2 m^{-2} day^{-1}.

For some locations in the Bay system we were able to make direct evaluations of the relative importance of SOC in total system respiration (total respiration = SOC + water column respiration). As previously reported by Kemp et al (1992) and others we found that the relative importance of SOC declined as a function of depth (Fig. 7-6). At the shallowest of sites (<4 m) SOC comprised 35-45% of total system respiration and decreased to about 20 -25% between 6 and 10 m and was 5-10% at the deepest sites. Boynton et al (2008; in review) found that SOC and other sediment processes accounted for about 30-35% of total system activity in the Patuxent, very close to the values predicted in Figure 7-4. We had available both sediment and water column respiration data for the Potomac River estuary and, because of the large depth range in this system we examined the SOC: total respiration ratio as a function of depth for this system as well. A similar pattern emerged here with 50-80% of system respiration being associated with sediments at depths < 4 m and less associated with sediments at greater depths. Again, even at substantial depths, SOC still remains an important sink term in oxygen budgets.

These analyses suggest a somewhat less important role of sediments in issues related to DO conditions in the Bay and a dominant role for water column respiration. However, this is probably not the case, especially at deeper stations. In these analyses we used total water column respiration rates. Specifically, we made respiration rate measurements using surface water and then extrapolated these volumetric rates to the full water column. Several words of caution are warranted regarding this extrapolation and the role of sediments in DO processes. First, we do not actually know if surface respiration rates are similar to those in deeper water; our suspicion is that deep water rates are likely lower because particulate organic biomass (algae and algal detritus) concentrations are lower. Thus, we may have underestimated the importance of SOC on DO dynamics. Second, we used the same extrapolation in vertically mixed as well as stratified sites. Water column respiration at stratified sites has a small effect on hypoxia above the pycnocline because these waters can be readily re-supplied with DO from the atmosphere. The water column respiration below the pycnocline does indeed have an effect on DO dynamics because there is no direct atmospheric re-aeration. Thus, by using total water column respiration at all sites we probably underestimated the relative importance of SOC at deeper and stratified sites. If routine measurements of respiration in surface and deep waters were instituted we could better define the relative roles of these two central processes in DO dynamics.

7-4. "Take-Home" Summary

- Despite a relatively small range in depths (1-42 m) strong relationships between depth and SOC were evident in the full data set and in selected areas of the Bay. This finding is consistent with several earlier examinations of this issue where a far greater range of depths were considered. The SOC-depth relationship appears quite robust
- The general explanation for this relationship is that the amount of euphotic zone organic matter which sinks to the sediment surface to support SOC decreases as longer water columns increase the transit time (and attendant opportunity for consumption by heterotrophic plankton) for sinking substrates. In short, in deeper water columns animals eat most of the sinking material before it gets to the bottom
- Water column respiration rates have been grossly under-measured in the Bay and tributary rivers. With available data it is clear, however, that water column respiration is a major term in oxygen budgets and deserves much more attention.
- As previously reported for other coastal and estuarine systems the relative importance of SOC compared to water column respiration is also a function of depth in Chesapeake Bay and tributary rivers. At depths < 4 m SOC dominated community respiration and the importance of SOC decreased with additional depth.
- Water quality models should be able to reproduce the empirical relationships between SOC, water column respiration and depth developed in this synthesis

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Chapter 8

Relationship of Sediment P Flux to pH and DO Conditions

8-1. Background and Sediment P Concepts

In this Chapter we consider general patterns of sediment P flux and focus on environmental factors that appear to exert strong control on these fluxes. Sediment phosphorus dynamics are of particular interest in estuarine environments because of the likely role sediments play in regulating the nutrient supply for primary producers, mainly phytoplankton, during warmer portions of the year when sediment processes are most active. There is now a convincing body of evidence, compiled from the scale of controlled (but not highly realistic) laboratory experiments, through more realistic but less controlled mesocosm studies to whole estuary experiments, that indicates that during the warmer portions of the year N tends to be the limiting nutrient in estuarine waters having some salt content. During winter and early spring light and P are more likely to limit phytoplankton production rates in these systems (Fisher et al 1992; Boynton and Kemp 2008). Sediment processes may play a pivotal role in this switch from P-limitation in tidal freshwaters in winter and spring to more general N-limitation. Specifically, it appears that in normoxic sediments a good deal of N is lost via denitrification. However, during warm periods of the year estuarine sediments often become hypoxic and tend to release substantial amounts of DIP, enough to make P-limitation unlikely in many situations, and release substantial amounts of N (as NH_4) because coupled nitrification-denitrification is blocked by hypoxic conditions. It is the purpose of this Chapter to explore controls on sediment P dynamics.

The mobilization of P from aquatic sediments can arise from a variety of mechanisms. In this Chapter, calcareous sediments (which have a considerably different biogeochemical behavior) are not considered because they are not a feature of Chesapeake Bay sediments. In Chesapeake Bay the chief mechanisms for sediment P release include:

- Low redox is a key part of P release from most aquatic sediments (i.e. Einsele 1936; Mortimer 1941). Under aerobic, neutral pH conditions, Fe(III) oxides in sediment retain DIP by physical-chemical adsorption (Krom and Berner 1980; Cornwell 1987). Iron oxides often have high surface areas and present a key barrier to diffusion of DIP to overlying water. In freshwater sediments, the efficiency of P release is not as high as in saline sediments (i.e. Caraco *et al* 1989) because of the importance of sulfate/sulfate reduction on the surface area of Fe(III) oxides. Keys to redox-related P release are 1) dissolved oxygen concentrations in overlying water, 2) organic matter metabolic rates which affect rates of P mineralization and redox zonation, 3) the influence of benthic organisms which can rapidly transport DIP out of sediments via their water pumping activities and 4) modifying factors such as temperature and concentrations of alternate electron acceptors such as nitrate.
- Animals such as bivalves may help P bypass sediment biogeochemical processes by direct excretion into the water column. Cornwell and Owens (1999) have directly observed this in lake sediments where cores with bivalves had > 10 fold

increases in DIP fluxes. Less is known about this mechanism and it will not be discussed further. We have very little Chesapeake Bay data where infauna and sediment flux measurements were made at the same time and because of this we will not attempt examination of this mechanism.

- Elevated pH can be an efficient mechanism of P release (Seitzinger 1991). The enhancement of P release under the elevated pH conditions found in eutrophic lakes results in enhanced DIP fluxes (i.e., Jensen and Andersen 1992; Xie *et al* 2003). There have been two studies of the pH effect on sediment P flux in Chesapeake Bay and these will be discussed in this section.

We have included two schematic diagrams, with detailed legends, showing the rather complex processes related to sediment redox conditions thought to influence estuarine sediment P flux (Fig. 8-1 and Fig. 8-2). We have emphasized redox controls on sediment P flux because this controlling factor seems far more common in Chesapeake Bay than the effects of elevated pH on sediment P flux.

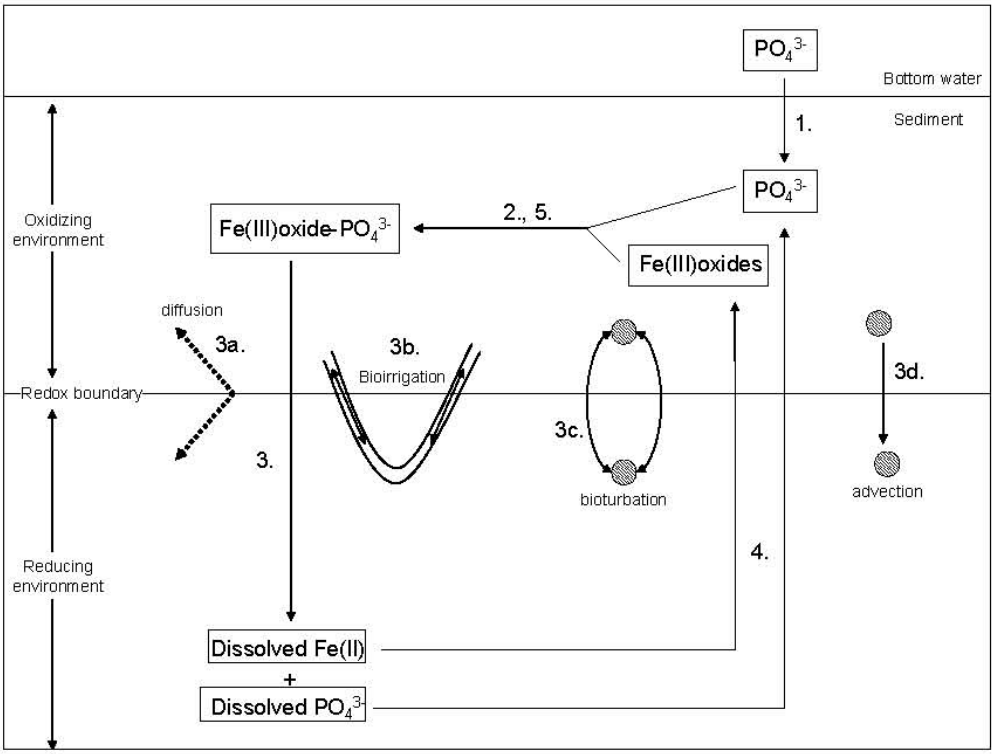

Figure 8-1. *Simple binding/release of P by Fe(III)oxides with varying redox conditions. 1) Phosphate from overlying water is incorporated into sediment porewater. 2) In oxidizing sediments, Fe(III)oxides bind PO4-3, making PO4-3 nonbioavailable. 3) Fe(III) oxides with bound PO4-3 are transported across the redox boundary to reducing sediments by a variety of mechanisms. In reducing sediments, Fe(III)oxides with bound* PO_4^{-3} *are dissolved to yield free Fe(II) and* PO_4^{-3}*. 3a) Diffusion is the movement of molecules down a concentration gradient in a fluid medium. Diffusion is more important*

for dissolved species like Fe(II) and free PO_4^{-3} than it is for the movement of Fe(III)oxides. 3b) Bioirrigation is the movement of porewater and its dissolved constituents due to the activity of benthic fauna (e.g. burrowing). Like diffusion, bioirrigation is more important for dissolved species than for sediment particles and minerals. 3c) Bioturbation is the movement of sediment particles and some porewater due to the activity of benthic fauna. 3d) Advection is the movement of sediment particles due to physical processes not mediated by benthic fauna. 4) Dissolved Fe(II) and PO_4^{-3} may be transported back to oxidizing sediments by the mechanisms discussed above. 5) In oxidizing sediments, Fe(II) is oxidized to Fe(III) and forms Fe(III)oxides, which may again bind PO_4^{-3}, retaining P in the sediments. This figure adapted from Bailey et al (2003).

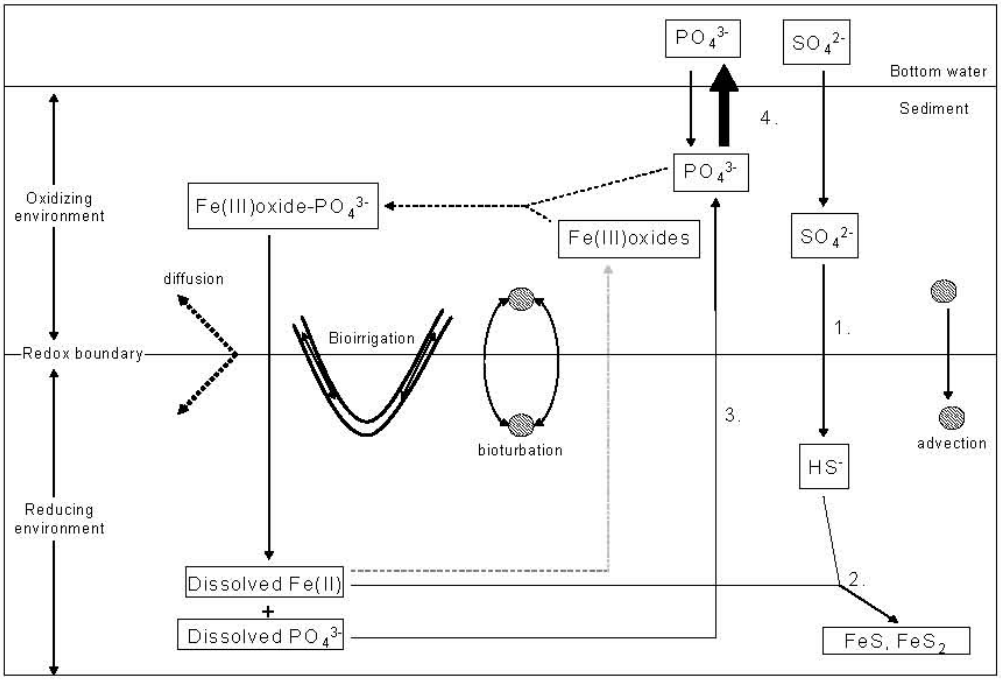

Figure 8-2. *The effect of S on binding/release of P by Fe minerals. 1) Sulfate reduction produces HS^-. 2) HS- and dissolved Fe(II) form iron monosulfides (FeS) and pyrite (FeS_2), sequestering Fe. 3) PO_4^{-3} is transported back to oxidizing sediments. 4) Since Fe is not available to form PO_4^{-3}-–binding Fe(III)oxides, PO_4^{-3} fluxes out of the sediments. This figure was adapted from Bailey et al (2003).*

8-2. Sediment P Flux in the Bay and Other Estuaries

Bailey (2005) compiled sediment flux data from 48 different estuarine sites (Chesapeake Bay data were not included) and examined these rates as functions of station depth, salinity and bottom water temperature (Fig. 8-3). Average rates ranged from about 2 to 75 µmol P m^{-2} hr^{-1}. Sediment P flux in this data set was highest at modest depths (5 - 10 m), modest salinity (5 -10) and at water temperatures in excess of 20 °C. Peak

sediment P flux in the low mesohaline (salinity = 5–10) region was probably a manifestation of both loosely sorbed P being released into solution as a consequence of

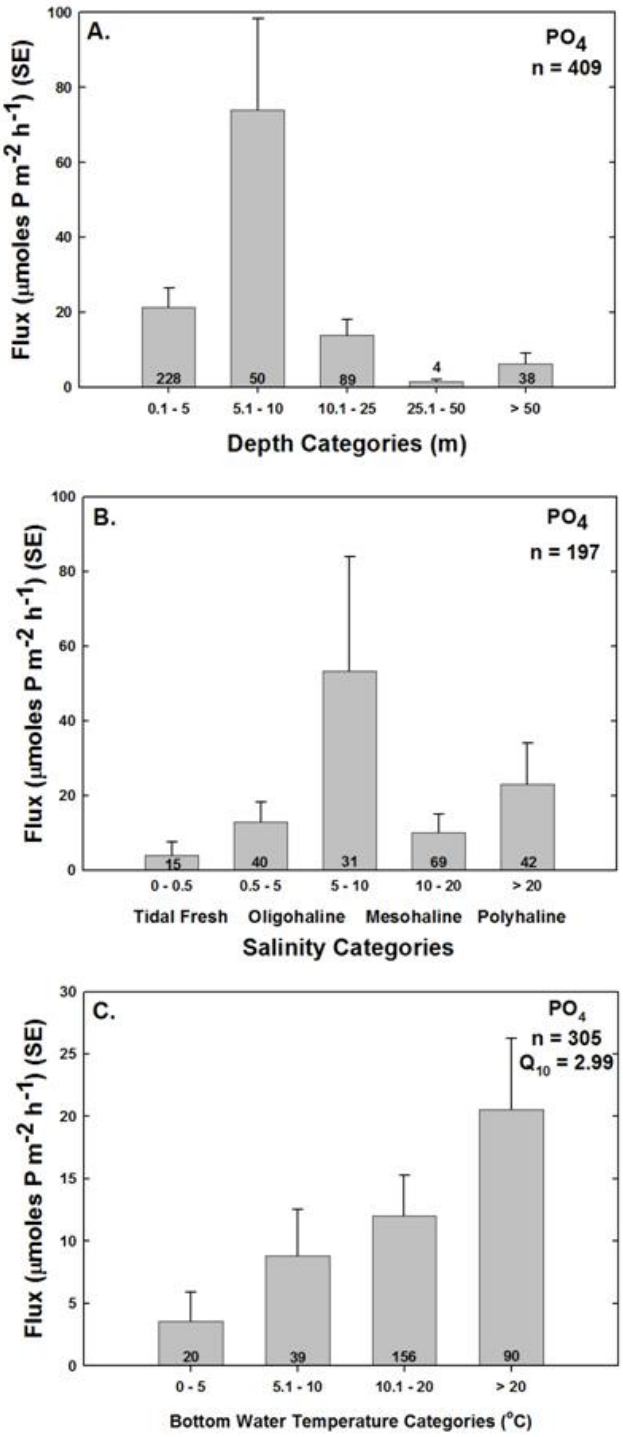

Figure 8-3. *Histograms of sediment P flux arranged by depth (a), salinity (b) and temperature (c). Data from Bailey (2005).*

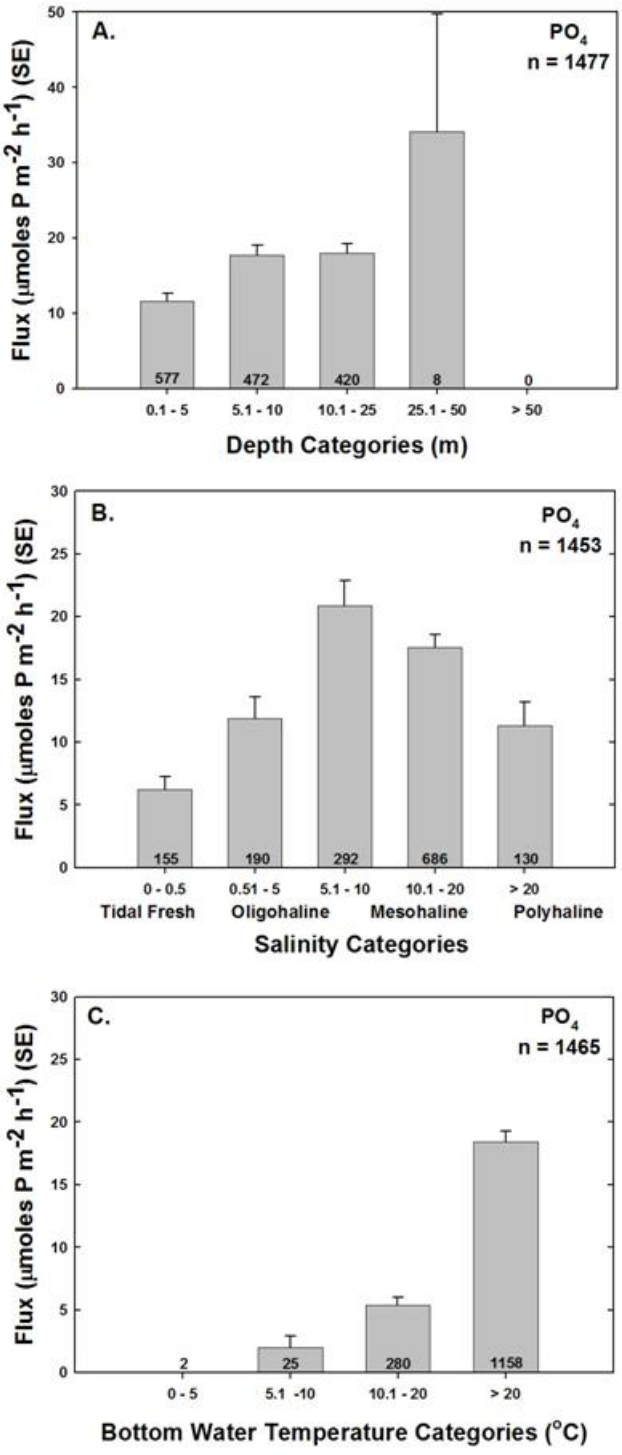

Figure 8-4. *Histograms of sediment P flux arranged by depth (a), salinity (b) and temperature (c). Data from the Chesapeake Bay sediment flux database.*

increased salinity (Froelich 1988) and of the dissolution of iron-phosphate complexes after chemical reduction of iron and precipitation of iron sulfides in anaerobic sediments

(Krom and Berner 1980; Jensen et al 1995). In general, sediment P flux tended to decline with water depth as plankton respiration causes a smaller percentage of sinking organic matter to reach the bottom due to longer transit times in deeper water columns, even for a relatively small depth range (0.2 – 50 m). However, mean fluxes (incubated in the dark) were lower at very shallow depths (0.2 – 5 m). The shallow water sediments are typically within the zone where autotrophic processes tend to dominate sediment biogeochemistry, with high rates of N and P assimilation by benthic algae and seagrasses and oxidized sediments which promote adsorbtion and precipitation of PO_4. Thus, PO_4 effluxes tend to be low in these shallow sediments. In addition, sediments and organic matter may be exposed to resuspension via wave action and the less dense labile organic particulates transported to deeper waters where they are remineralized. We should note the flux-depth pattern observed with this data set is not consistent with several other analyses including those of Nixon (1981) and Seitzinger and Giblin (1996) where depth ranges of 3-70m and <200m, respectively, were examined and did not exhibit strong relationships with depth.

Chesapeake Bay sediment P flux in relation to these variables was similar for salinity categories and temperature but very different regarding depth. In the Chesapeake Bay data set, sediment P fluxes increased with depth (Fig. 8-4). We suspect that this pattern in the Bay and tributary rivers results from the fact that many deep water sites in the Bay are chronically hypoxic and are thereby characterized by high sediment P fluxes.

8-3. Redox/Hypoxia Effects of Sediment P fluxes

Phosphorus dynamics at the sediment-water interface are subject to multiple controls. In this section redox potential in surficial sediments is examined. In oxidizing sediments (i.e., sediments with high Eh values), phosphate may bind to or co-precipitate with iron (or aluminum) oxyhydroxide minerals (Sundby *et al* 1992). In the sorbed or bound state, phosphorus remains in the sediments and is non-bioavailable. However, if the environment becomes reducing (i.e., low Eh values), or if newly formed Fe-P minerals are transported to more reducing zones of the sediment column (via advection, diffusion, bioturbation, or sediment accretion), phosphorus may not remain bound. Fe(III) oxides dissolve in reducing environments, releasing Fe(II) and P to the porewater. Porewater Fe(II) and phosphate may diffuse back up to more oxidizing sediments, where Fe(II) is reoxidized to Fe(III). If this occurs, phosphate is again bound by Fe(III) oxides and is thus retained in the sediments (Fig. 8-1).

However, if Fe(III) oxides are not again made available, due to reducing conditions or the presence of sulfur, P remains in the dissolved phase and is released from the sediments to the water column (Fig. 8-2). High sediment-water P fluxes are often observed in reducing environments. For example, P releases as high as 148 μmoles m^{-2} h^{-1} have been measured in the mid-Chesapeake Bay during summertime anoxic events (Cowan and Boynton 1996). Despite observations of high P fluxes in reducing environments, anoxia does not *always* result in P release from sediments, and oxic conditions do not necessarily result in P retention (Gachter and Muller 2003). Release of P from sediments depends not only on redox conditions, but also on the amount of Fe available to bind P, which is controlled by the precipitation and dissolution of iron sulfur minerals.

Iron sulfur mineral formation reduces the amount of Fe available to bind phosphate in sediments. Sulfate is one of the most abundant ions in seawater, and microbial sulfate reduction to sulfide is ubiquitous in estuarine sediments (Cornwell and Sampou 1995). Sulfide and reduced iron form iron monosulfides (FeS), and eventually pyrite (FeS_2). Iron monosulfides may be reoxidized to Fe(III) and sulfate, but pyrite is generally subject to more permanent burial (Cornwell and Sampou 1995). In either form (FeS or FeS_2), iron is not available to bind phosphate. Iron phosphate mineral formation can occur only if the Fe:P ratio is sufficiently high. Iron sulfide mineral formation lowers this ratio, but is dependent on the availability of S. Thus, the presence of sulfur increases Fe-S mineral formation and impedes Fe-P mineral formation, resulting in higher P fluxes out of sediments.

We have organized sediment P flux data from several sites in Chesapeake Bay that experience very low DO concentrations and low sediment Eh conditions during summer periods (Sta. RGPT in the mesohaline Potomac, R64 in the mesohaline mainstem Bay and BRIS in the mesohaline Patuxent). There is a strong tendency for sediment P flux to be quite low at elevated bottom water DO concentrations (> 4 mg l^{-1}) and elevated at lower DO concentrations (Fig. 8-5). Since sulfate is abundant at all these sites, it is probable that the S - Fe - P reactions described above are responsible for this pattern of sediment P flux. To place the magnitude of sediment P flux under reducing

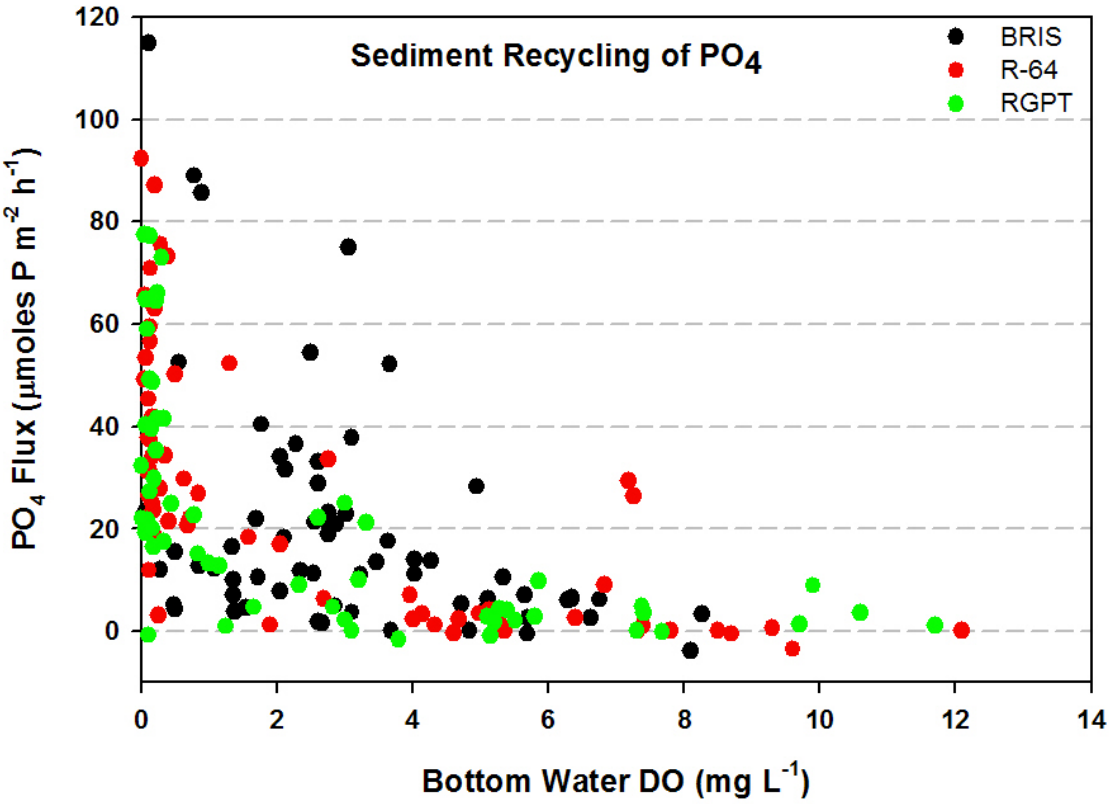

Figure 8-5. *Scatter plot of bottom water DO concentration versus sediment PO_4 flux. Data were from mesohaline portions of the mainstem Chesapeake Bay (R-64), Potomac River estuary (RGPT) and Patuxent River estuary (BRIS).*

conditions in some perspective, a P flux of about 40 µmol P m^{-2} hr^{-1} (average of fluxes at bottom water DO conditions < 4 mg l^{-1}) could support phytoplanktonic P demand at rates of about 1.2 g C m^{-2} day^{-1}, a very considerable production rate. We can also compare these sediment P fluxes to inputs of "new P" from landside sources. In this case, Chesapeake Bay P loads range from about 0.3 to 2.4 g P m^{-2} yr^{-1} (Boynton et al 1995). Converting anoxic water sediment P flux to these units yields a rate of about 11 g P m^{-2} year $^{-1}$, 5 to 35 times larger than new inputs of P. Of course, these high rates of sediment P flux are not maintained all year. However, even when only the warm half of the year is considered, these rates are large compared to inputs of P from landside sources. Additionally, the form of P released from sediments (DIP) is directly utilizable by plankton whereas P from uplands is largely (> 65%) particulate inorganic P (PIP) and this P is not directly available to the biota.

This issue of sediment P release under conditions of degraded water quality is of central importance to management. The message seems rather simple and is largely captured in Figure 8-5. In short, if bottom water DO concentrations can be elevated during summer periods to 3-4 mg l^{-1} sediment P flux would likely decrease by a large margin. This, in turn, would have the effect of adding to nutrient limitation of phytoplankton production. This negative feedback process is also shown in Figure 1-1.

We also have limited information regarding the responsiveness of estuarine sediment P flux to changes in bottom water DO and sediment redox conditions based on controlled laboratory measurements. Jasinski (1996) obtained sediment cores from the

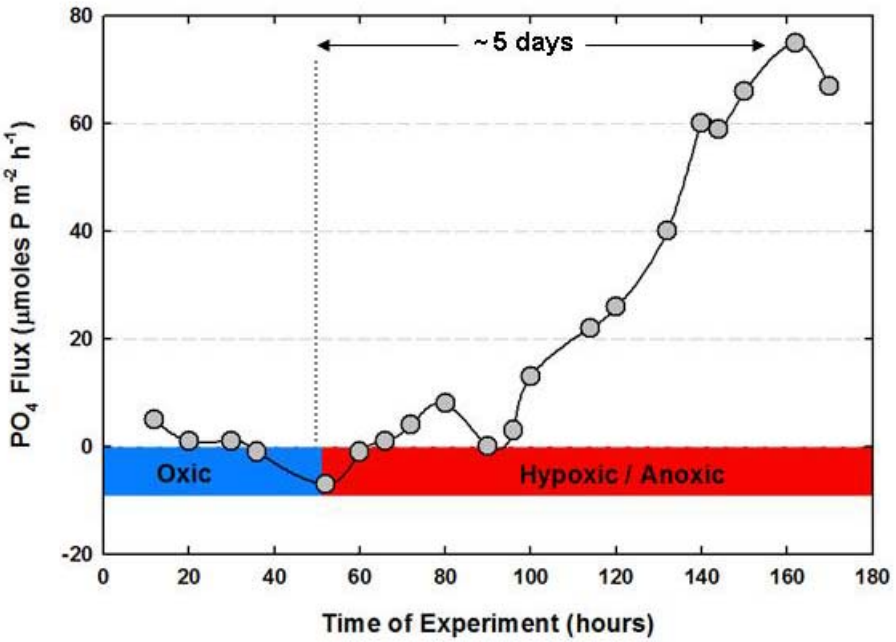

Figure 8-6. *Results of experimental DIP flux studies conducted by Jasinski (1996). In these studies sediment cores were collected from the mesohaline mainstem Chesapeake Bay immediately after spring bloom deposition (May). Cores were incubated in the dark at 20°C for 4 days with normoxic overlying water. Overlying water was then stripped of DO and the DIP (PO_4) fluxes were measured under near-axoxic conditions. Maximum DIP flux occurred after 5 days exposure to anoxic conditions.*

mesohaline mainstem Bay in spring (May) shortly after deposition of the spring diatom bloom. Thus, these sediment were "charged up" with labile organic matter and had not been exposed to anoxic conditions since the pervious summer. These cores were then placed in a laboratory environment where temperature was slowly elevated to 20 °C. After about 4 days of exposure to normoxic overlying water, DO concentrations were reduced to about 0.2 mg $^{-1}$ (severe hypoxia). Sediment P flux measurements were made repeatedly for about 20 days and these measurements indicated several things (Fig. 8-6). First, sediments were quite responsive to a large change in DO conditions of overlying waters. Sediment P flux began increasing about 2.5 days after DO concentrations decreased and peak sediment P releases were observed after 5 days. These fluxes then slowly decreased for the next 15 days and reached low levels (< 5 μmol P m^{-2} hr^{-1}) after about 40 days. These results again suggest a sediment surface responsive to water quality conditions and further indicates a rather limited "P memory" in these sediments.

8-4. Elevated pH and Sediment P Flux

A second mechanism of sediment P release involves pH conditions in overlying waters and in sediment pore waters. It has long been suspected (e.g. Seitzinger 1991) that P derived from tidal freshwater estuarine sediments might play a central role in supplying P needed to stimulate and maintain algal blooms (e.g., *Microcystis aeruginosa*) in Chesapeake Bay tributaries, particularly in the upper region of the tidal Potomac River estuary.

Under increased pH conditions (>9.0), P adsorbed to Fe(III) oxides can be released into solution. There have been, it appears, relatively few investigations of pH influences on sediment P flux in estuarine systems. Such investigations have been conducted in lakes and it appears that pH influences are clearly operative (e.g., Anderson 1974; Istvanovics 1988). In the case of estuarine systems such examinations have rarely been conducted, probably because in most estuaries there is sufficiently strong carbonate system buffering to prevent pH increases to the extent needed for sediment P responses. Because of this, pH was not routinely measured during many of the Chesapeake Bay sediment flux monitoring programs. However, in a few instances, most notably during Potomac River estuary sediment flux monitoring, pH was added as a routine variable and measured in the water column at appropriate depths.

The earliest study of pH effects on sediment processes was conducted in the upper Potomac River estuary. Seitzinger (1991) conducted a series of pH enhancement measurements using sediment microcosms with pH control using direct additions of a strong base. Results indicated that sediment P fluxes were small (< 25 μmoles m^{-2} hr^{-1}) when pH was <9.0. At some sites sediment P fluxes increased when pH was elevated to 9.5 and all sites exhibited larger sediment P fluxes at a pH of 10. Increases in pH to 10.5 did not further increase sediment P release rates.

A study of P distribution along the Delaware Estuary provides an example of the impact of pH on P dynamics (Lebo and Sharp 1993). In that study, Delaware River estuary total (TP), particulate (PP) and dissolved inorganic (DIP) phosphorus data from 1970 to 1990 were compared. Data indicated a large decrease in TP throughout the estuary during this period, but also showed a significant *increase* in DIP near Philadelphia. The increase in DIP was attributed to desorption of PP due to increased pH, which was most likely the result of phytoplankton blooms which developed after two

Philadelphia wastewater treatment stations upgraded from primary to secondary treatment (secondary treatment effluent is rich in inorganic N and P). The Delaware Estuary study demonstrated that localized changes in pH can have a profound impact on P dynamics. The Delaware study also serves as a reminder about the existence of internal sources of bioavailable P, such that reduced P loading to an estuary may not be immediately accompanied by corresponding reductions in bioavailable P.

During 2004 three sediment P flux - pH experiments were conducted in the upper Potomac River estuary (Bailey et al 2006). Here we highlight major findings and refer the reader to Bailey et al (2006) for detailed discussion of pH effects on sediment P flux. In the first experiment a single pH level was selected (pH = 10), sediment cores collected from several locations in the upper tidal Potomac during spring, and sediment P fluxes measured after 5 and 7 days of incubation. Except for the fact that different methods of pH adjustment were utilized, these measurements were conducted in a fashion similar to those of Seitzinger (1991). Ambient (i.e., non-pH adjusted cores) fluxes were very small, fluxes were larger after 5 days exposure to elevated pH and after 7 days fluxes were very

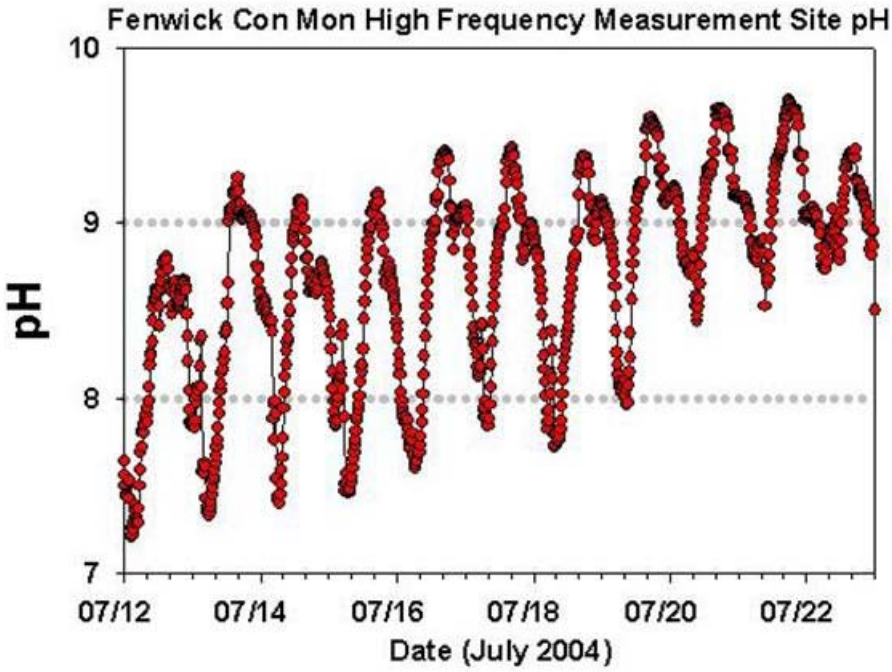

Figure 8-7. *A time series (12-23 July, 2004) of pH measurements from a shallow, shore line site (Fenwick) in the upper Potomac River estuary. Measurements were made 1 m below the surface. Data from http://mddnr.chesapeakebay.net/eyesonthebay/index.cfm.*

substantial at all sites. Thus, these results indicate that the potential for elevated sediment P release is high during spring throughout the upper Potomac. This approach, however, teaches us little about the time-course of pH effect on estuarine sediments other than after an extended period of exposure sediment P fluxes can be large. During July 2004 additional sediment cores were collected from the same area of the Potomac and exposed to ambient pH conditions, pH 9.6 and pH 10.5 with sediment P flux measurements made as a time-series during a 5 day period in all treatments. In this case there was a clear

indication of response to pH elevation almost immediately (2 hrs post-treatment) for both the pH 9.5 and 10.5 treatment cores. Sediment P fluxes did not respond further in the pH 9.5 treatments but continued to increase to extremely high levels (> 100 µmoles m^{-2} hr^{-1}) in the pH 10.5 treatment core after 48 hours of exposure. Thus, these data suggest that response to pH can be very rapid, well within the diel pH cycle observed with shore-based high frequency measurement systems (Fig. 8-7), and that the magnitude of response is proportional to the degree of pH elevation. The final experiment utilized sediment cores collected in early fall and exposed to pH conditions of 9 and 10. For reasons that remain unclear, sediment P flux responses to pH elevation were not consistent. The time-series of response fluxes at some sites were quite small and at others the pH 10 treatment elevated sediment P fluxes but not to the same degree as did similar pH treatments in summer. These results suggest some significant seasonality in the potential for sediments to respond to elevated pH conditions.

While there were temporal and spatial differences in sediment P fluxes in response to pH elevation there were also strong patterns of pH response when the full sediment flux data set was examined as a function of pH. In Figure 8-8 and experimental sediment P fluxes were plotted as a function of pH at the time of measurement. Data from May, July and September are color coded and *in situ* measurements are indicated by circles and experimental measurements indicated by triangles. With very few exceptions,

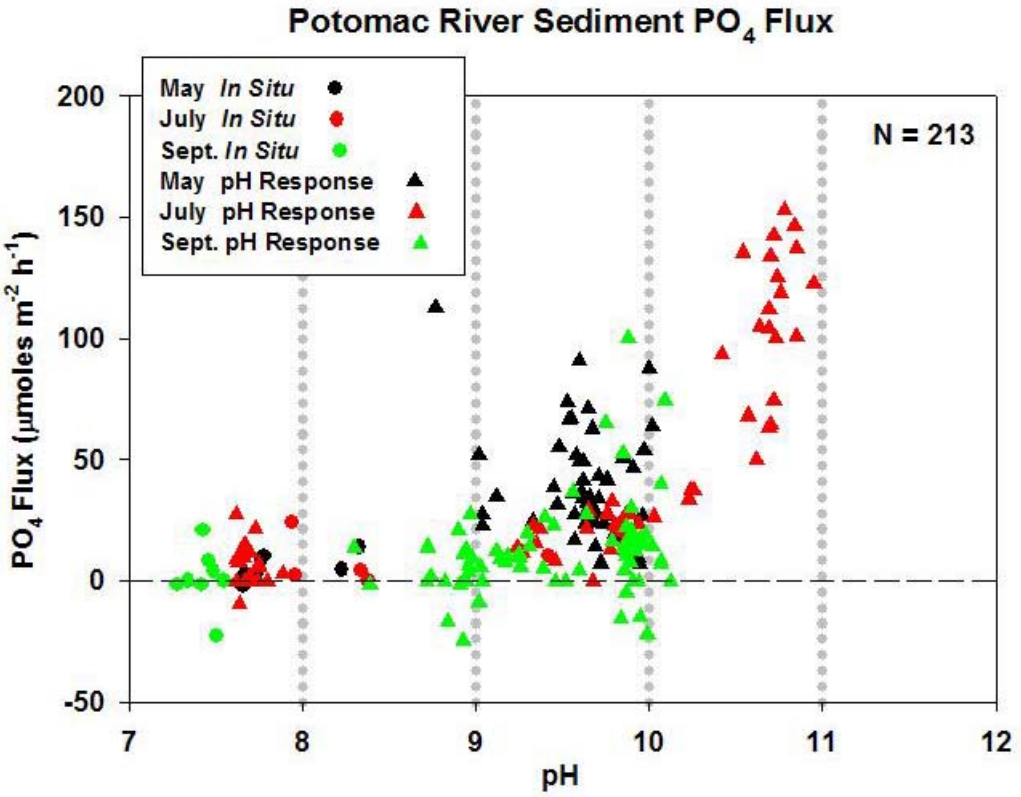

Figure 8-8. *A scatter plot of sediment P flux as a function of water column pH. In situ fluxes are shown as circles and experimental fluxes are triangles. Month of measurement is color coded. These data were from Bailey et al (2006).*

sediment P fluxes were low (< 25 µmoles m^{-2} hr^{-1}) at pH levels less than about 9.2. In fact, the majority of these fluxes were less than about 10 µmoles m^{-2} hr^{-1} and about 50% were either zero or were directed into sediments, again at small rates. We make this point because at these pH levels (7 -9) sediment P fluxes are not sufficient to support major phytoplankton bloom formation. However, under pH conditions higher than about 9.2, sediment P fluxes did increase and at pH levels of between 10.5 and 10.9 reached very high levels capable of supporting very large phytoplanktonic nutrient demand. There is also an indication of temporal variability. Experimental measurements made in July responded to pH elevation more than did cores similarly exposed in May. Measurements made in September responded least to pH increases. Some of this variability might be associated with *in situ* conditions prior to measurement, seasonal variation in sediment P availability, seasonal variations in sediment structure, animal community characteristics influencing bioirrigation or some other factor, or combination of factors, we have yet to consider. However, there remains the fact that there was a strong experimental response to elevated pH and the magnitude of the response was sufficient to supply a great deal of P to the water column.

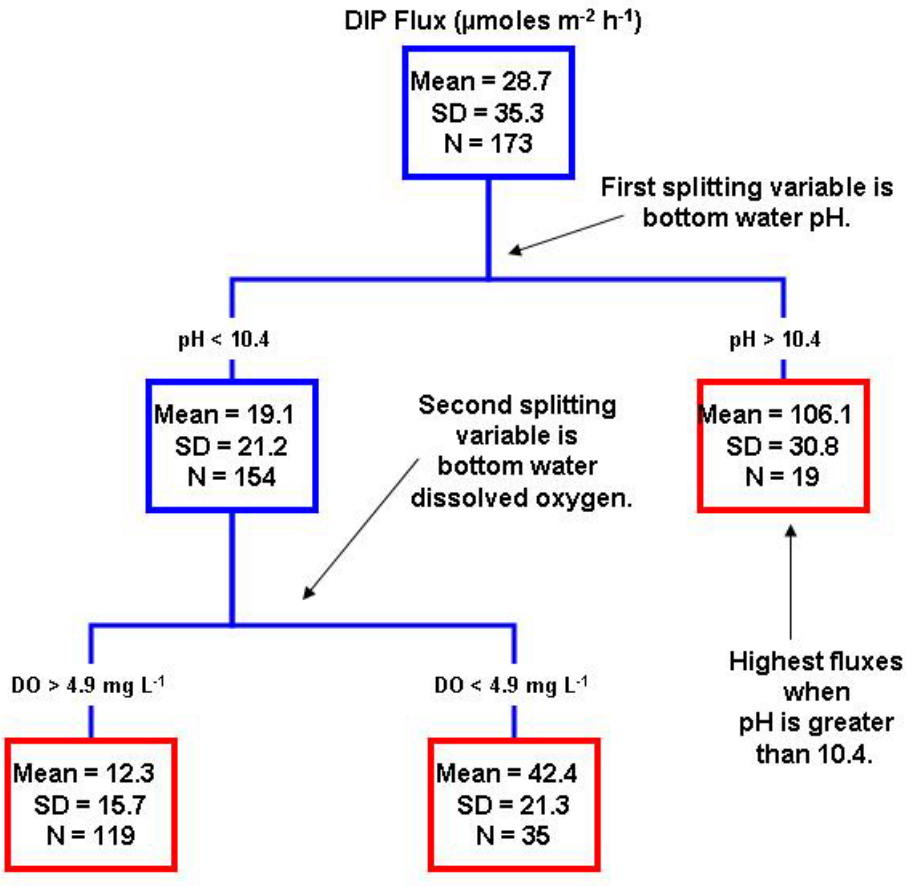

Figure 8-9. *Preliminary results of classification and regression tree analysis focused on factors influencing DIP flux in the Potomac River estuary. These data taken from Bailey et al (2006)*

One of the issues yet to be fully addressed concerns spatial and temporal prediction of sediment P and other fluxes. There have been some successes in modeling sediment biogeochemistry (see, for example, DiToro 2001 for a review of simulation modeling approaches). In Chesapeake Bay, Cowan and Boynton (1996) found very strong statistical relationships between the amount of labile organic matter at the sediment surface during spring (following deposition of the spring phytoplankton bloom) and subsequent oxygen, nitrogen, phosphorus and silica fluxes during summer along the salinity gradient of mainstem Chesapeake Bay. Later, Cowan *et al* (1996) extended these analyses to include data from Mobile Bay with similar results. More recently, Stankelis *et al* (1998) developed multiple regression models of sediment nutrient fluxes for the mesohaline portion of the Patuxent River estuary and important predictive variables included sediment redox status, bottom water oxygen and nutrient concentrations, and sediment organic matter content. However, neither of these studies included tidal freshwater portions of the estuary. We have examined the Potomac River estuary portion of the full data set for relatively simple, useful statistical models for predicting sediment P releases (or uptake). As an exploratory step we have used a technique called Classification And Regression Tree (CART®) analysis which is a non-parametric multivariate approach for prediction of both categorical (classification) and continuous (regression) variables. Within these analyses both categorical and continuous predictors can be used. We used the TREES module in the Systat® 10.2 software package with the least squares estimate for the loss function. The result of sediment P flux analysis is provided in Figure 8-9. Major "splitting factors" classifying sediment P flux was water column pH (first splitting variable) and bottom water dissolved oxygen concentration (second splitting variable). In both cases, mechanistic explanations are available. The pH influence has already been discussed in previous sections of this report. Dissolved oxygen concentration is likely an indicator of redox conditions in the surficial sediments where more reduced sediments (as indicated by lower water column dissolved oxygen concentrations) favor larger sediment P release rates. We hope to further elaborate these analyses in the future with the ultimate goal being multivariate models useful in prediction of sediment P fluxes based on readily measured water column and sediment properties.

8-5. Potomac River Sediment P Flux Patterns

Unfortunately, there are not many tributary locations in the Chesapeake Bay flux data set where there are measurements of sediment P flux across a large salinity gradient. In upper Bay tributaries were is not much of a salinity gradient and some are primarily tidal freshwater systems. A great many sediment P flux measurements have been made in the Patuxent River estuary but the vast majority were made in the mesohaline zone. The limited number of sediment flux sites in the Choptank River estuary precludes salinity/sediment flux investigations. One place where detailed axial measurements of flux across a large salinity gradient are available is for the Potomac River estuary.

Sediment P flux data from several Potomac River estuary studies were combined and plotted as a function of the full estuarine salinity regime to further explore the role of sediments as a source of P available to support algal bloom formation (Fig. 8-10). In this diagram P fluxes were low (~ 10 μmoles P m^{-2} hr^{-1}) in the tidal fresh region and in the low mesohaline region and about 2 and 2.5 times higher in the oligohaline and high

mesohaline zones, respectively. The two regions of elevated P flux correspond to the region of most intense algal bloom formation and to the region characterized by severe summer season hypoxia/anoxia, respectively. In the first case there is the possibility that bloom formation elevated pH sufficiently so that P was released from Fe-rich sediments and became available to support further bloom growth/persistence. We have assembled a conceptual model of the chain of cause-effect linkages possibly leading to a self-reinforcing cycle of high pH and high sediment P releases in weakly buffered oligohaline zone of the estuary (Fig. 8-11).

In the high mesohaline area of the estuary high sediment P releases were very likely caused by reactions between reduced S and iron-bound P wherein P is released into solution and moves from sediment porewater into the water column. Thus, in this estuary there may be two zones prone to high P release from sediments and the mechanisms of release involve elevated pH in the low salinity zone and hypoxia/anoxia in the higher salinity zone. We suspect that the high pH mechanism is not generally important because the areas of the Bay where very high pH values can be attained are limited. This mechanism is far more important in poorly buffered and eutrophic lakes.

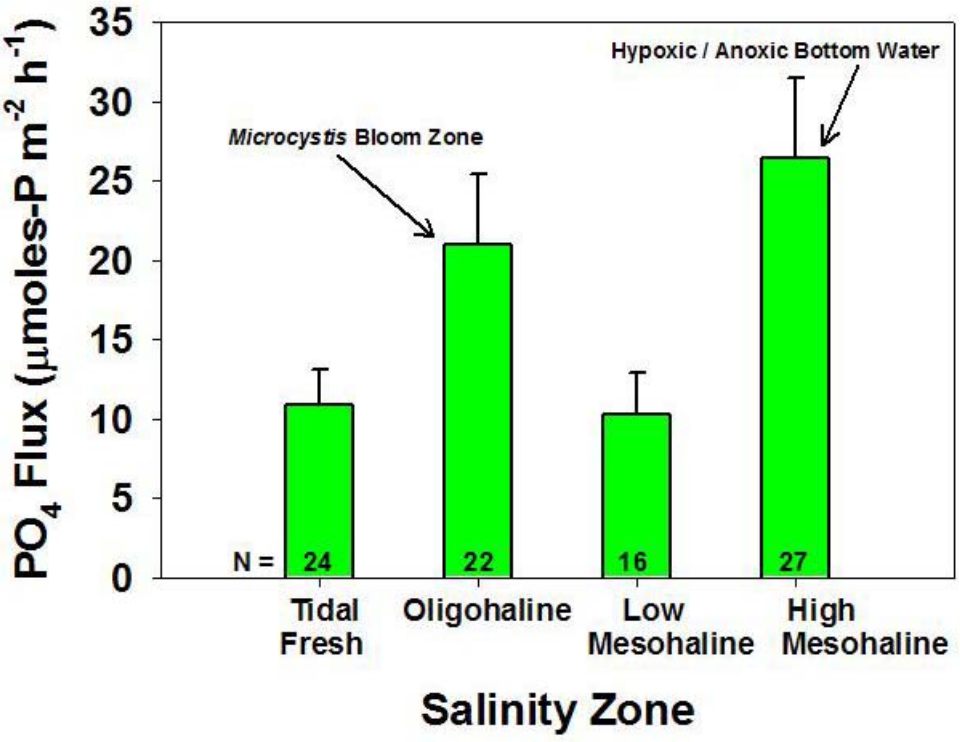

Figure 8-10. *A summary of in situ Potomac River estuary fluxes of phosphorus during warm seasons collected along the Potomac salinity gradient. Data were from Callendar (1982), Bailey et al (2003) and Bailey et al (2006).*

To provide some comparison to the spatial pattern of sediment P flux along the salinity gradient of the Potomac River estuary we have assembled all summer sediment P flux data from the Chesapeake Bay flux data set and plotted these as a function of salinity (Fig. 8-12). Mean sediment P fluxes were similar to those measured in the Potomac. However, there was no indication of elevated sediment P flux in the oligohaline regions

of all Chesapeake Bay sites (probably because pH was not sufficiently elevated as it can be in the Potomac). However, average sediment P flux was elevated, (> 20 µmol m^{-2} hr^{-1}) at all salinity zones from 5 to 20, similar to the situation in the Potomac. It is likely that low sediment redox conditions contributed to generally high sediment P flux in the large data set as it did in the Potomac. Somewhat lower sediment P releases at salinities above 20 is likely related to better water quality conditions in the high salinity portion of the Bay and lower organic matter delivery rates to sediments in the less eutrophic high salinity regions.

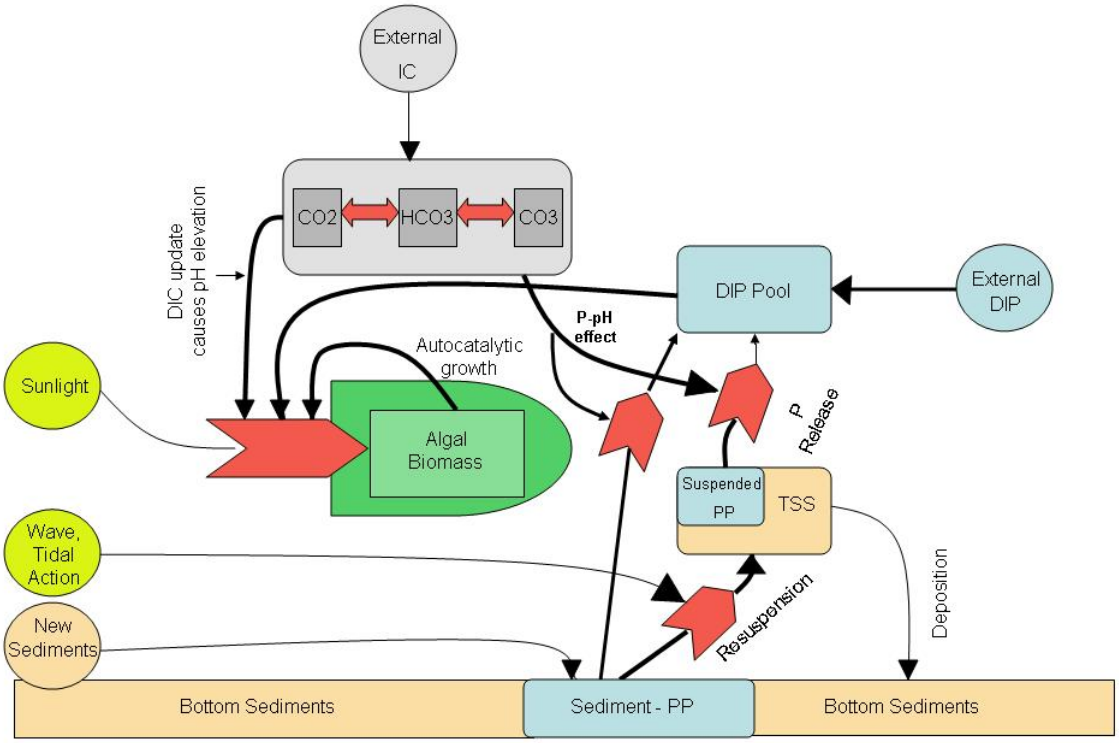

Figure 8-11. *A conceptual model focusing on pH influence on P dynamics in sediments and the water column and showing the autocatalytic nature of these processes.*

8-6. "Take-Home" Summary

- The Chesapeake Bay sediment flux data set contains 1480 measurements of sediment P flux made in a broad variety of depth, salinity, trophic state, and temperature conditions.
- During summer periods sediment P releases can have a large impact on water quality conditions. It appears that in areas of the Bay and tributary rivers with some salt content in overlying waters sediment P fluxes can supply enough P to support modestly high rates of plankton production. These rates are as large (or larger in some cases) than input rates of P from terrestrial sources and sediment P releases are in a chemical form (DIP) ready for immediate utilization by biota.

- It appears that sediment P flux is greatly enhanced under poor water quality conditions of low DO in bottom waters and low sediment redox conditions.
- In a few localized areas of the Bay (e.g., upper Potomac River estuary) elevated water column pH can lead to elevated sediment P releases. We do not think this is an important mechanism in most areas of the Bay because waters are well buffered against large pH changes.
- Limited experimental work indicates that sediments are responsive, on short time scales (hours to a few days) to changes in both pH and sediment DO and redox conditions. Sediments responded to sharply increased pH in a matter of hours and to very depressed DO conditions in 2-3 days.
- While there appears to be a large stock of P in sediments, experimental studies indicated that sediments from the mesohaline mainstem Bay could be depleted in available P in a matter of a month or a little more when exposed to very low DO conditions and no new organic matter or sediments reaching the sediment surface. This suggests that the sediment P memory is not long as is the case in many eutrophic lakes.

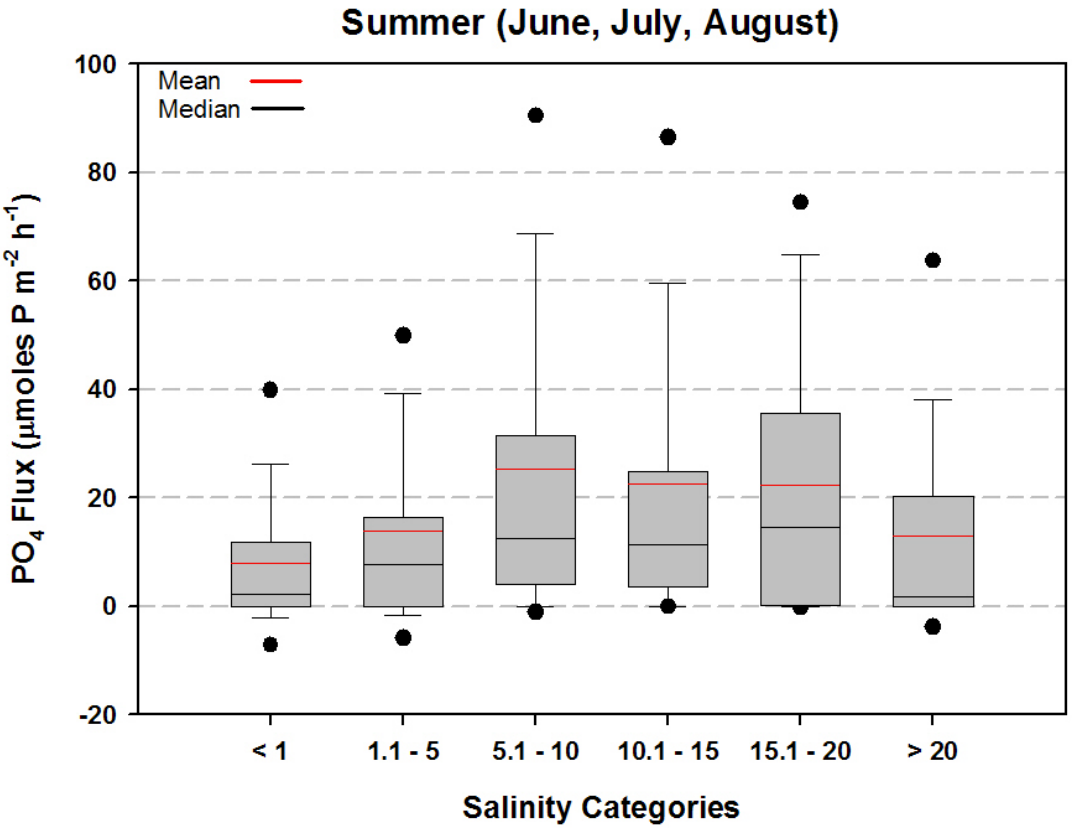

Figure 8-12. *Box and Whisker plots of sediment P fluxes as a function of bottom water salinity categories. All data in the Chesapeake Bay sediment flux dataset were included in this diagram.*

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Chapter 9

Flux Relationships to External Nutrient Loads

9-1. Background and Concept

We have argued, as have many others (Rabalais 2000; Kemp et al 2005) that nutrient loading rate (mainly N and P) is a primary determinant of estuarine trophic status. We have further argued that there are both simple chains of causation related to estuarine eutrophication as well as complex positive and negative feedback processes (e.g., Fig. 1-1; Kemp et al 2005). Estuarine sediment processes play a role and, at times, a rather dominant role, in estuarine eutrophication. In this Chapter we relate external nutrient loading rate (primarily N loading) to sediment fluxes using time-series data from a few Chesapeake Bay sites and comparative analyses involving multiple Chesapeake Bay sites.

We begin by presenting a conceptual model relating river flows, and associated nutrient loads, to sediment processes (Fig. 9-1). In this diagram river flows are shown as having three dominant effects and these include geographic positioning of salinity regimes as a function of flow (i.e., in heavy flow years, tidal freshwater zone covers a

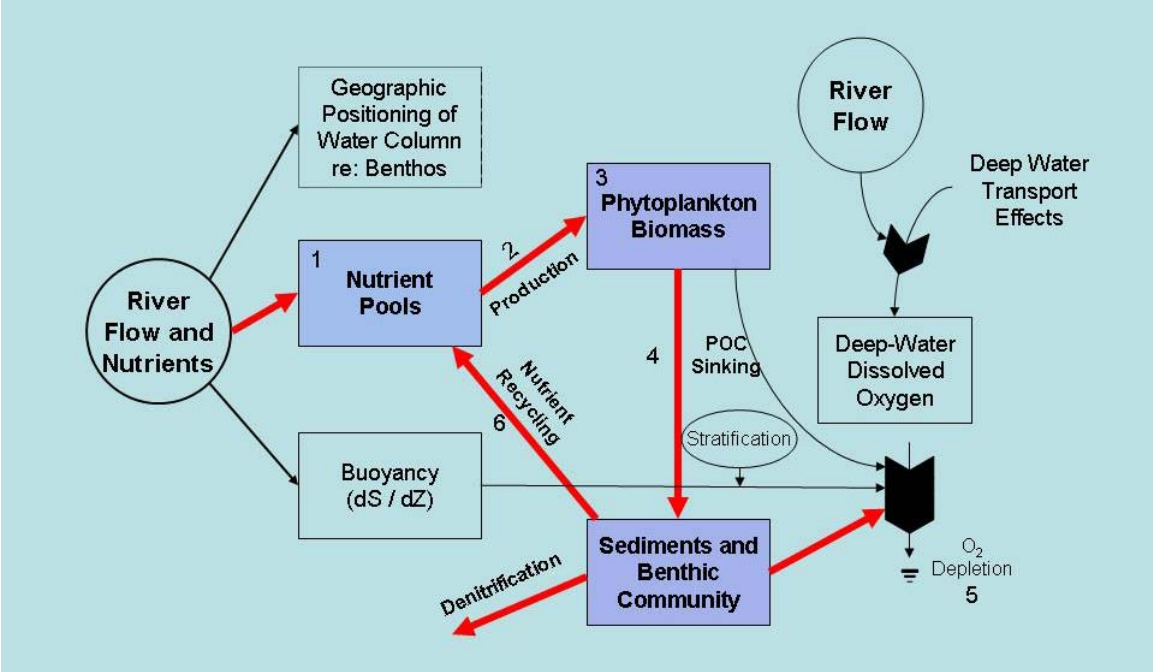

Figure 9-1. *A simple schematic diagram showing the influences of river flow (and associated nutrients) on a variety of ecosystem storages and processes. Some mechanistic relationships are shown in the diagram and thus explained in the text. This figure was adapted from Boynton and Kemp (2000).*

large area of the benthos), nutrient additions to the estuary and water column buoyancy. A portion of the nutrient pool (DIN and DIP) is readily available for autotrophic uptake and we have shown an example of Chesapeake Bay phytoplankton responding to variations in nutrient loads. The load - production (and load - algal biomass

accumulation) relationship has been well developed for freshwater systems (e.g., Schindler 1981; Vollenweider 1976) and has now been well developed for estuarine and coastal marine systems (e.g., Boynton et al 1982; Nixon 1981). Boynton and Kemp (2008) have assembled over a dozen simple statistical models of this relationship based on estuarine data. In the conceptual model phytoplankton biomass is shown as sinking to the sediment surface. In most estuaries this is a poorly documented rate process. However, in Chesapeake Bay several studies have managed to capture this flux and we have included analyses of those data in this chapter. Sediments are shown to recycle inorganic nutrients back to the water column as well as consume oxygen in the process of decomposing deposited organic matter. Finally, some nitrogen is shown as being lost from the system via denitrification. We have included this Chapter because it is important to understand that sediment processes respond to nutrient loading rates as well as influence water quality conditions within the estuary.

9-2. Water Column Production, Organic Matter Deposition and Sediment Processes

Research efforts (noted earlier) have developed strong relationships between nutrient loads from terrestrial and atmospheric sources and estuarine plankton production

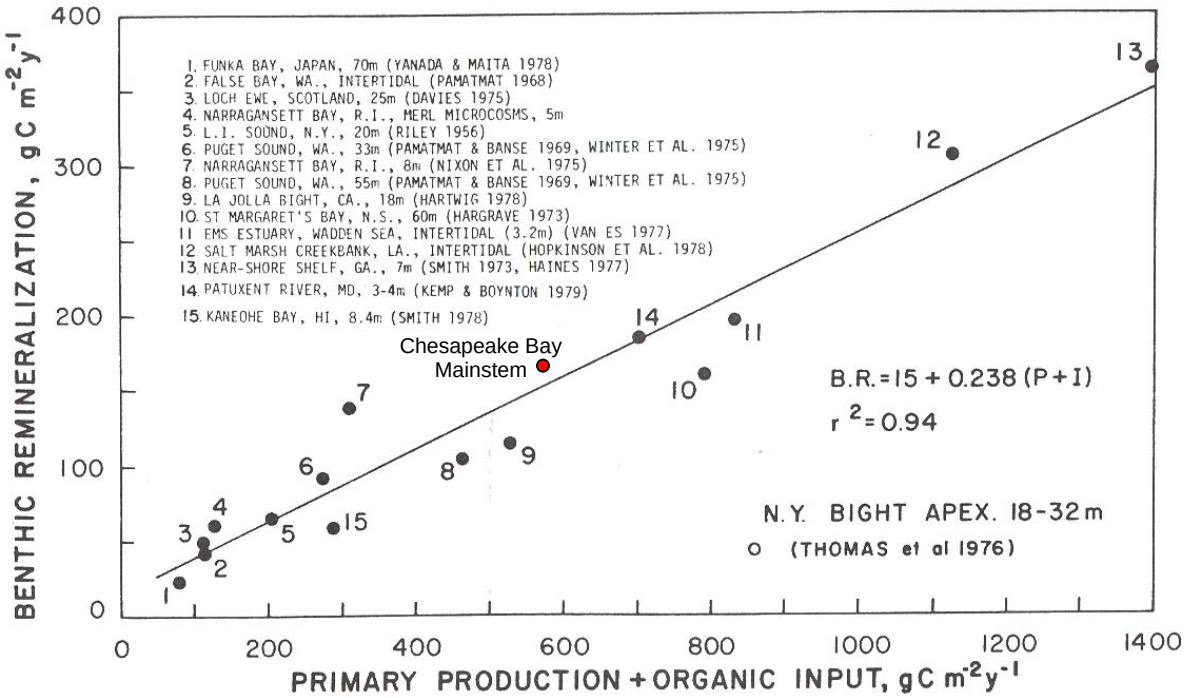

Figure 9-2. *Results of a linear regression analysis relating organic matter production in the water column to benthic use of deposited organic matter. Data are from a variety of estuarine and coastal marine systems. This relationship represents one portion of benthic-pelagic (B/P) coupling relating organic matter produced in the water column to sediment consumption of organic matter. This diagram was adapted from Nixon (1981).*

and we will not repeat those here as this is not the primary focus of this report (see Boynton and Kemp 2008). However, the next step in the cause -effect linkage (Fig. 9-2) involves organic matter availability and sediment responses. One of the earliest and best known analyses of this linkage was developed by Nixon (1981) and shows a strong and

linear relationship between primary production (plus detrital carbon input from rivers) and sediment remineralization rate of organic matter deposited to sediments. There is a substantial range for both variables spanning estuarine systems that could be classified as oligotrophic to very eutrophic. Sediment flux (measured as SOC and converted to C

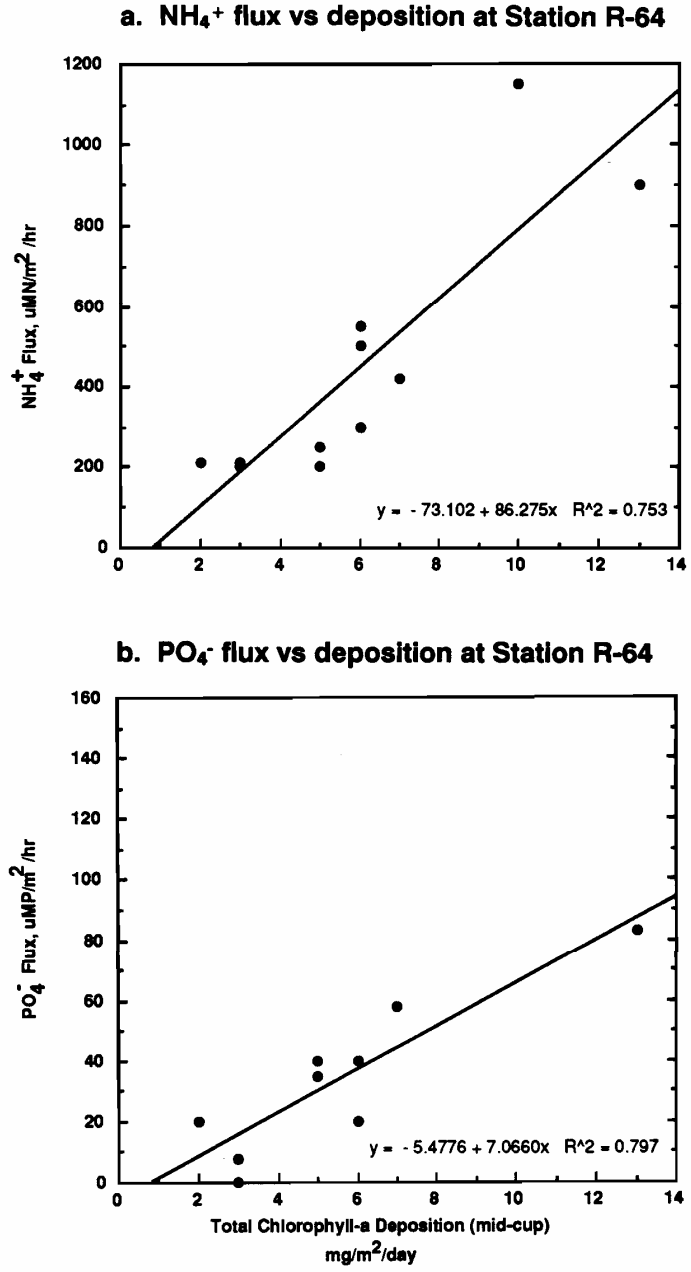

Figure 9-3. *Scatter plots relating time-lagged sediment fluxes of NH_4 (a) and PO_4 (b) to total chlorophyll-a deposition rates at a mesohaline site in Chesapeake Bay. The lags relate to spring-summer deposition rates and summer sediment fluxes (Boynton et al 1992).*

units) in the mesohaline portion of mainstem Chesapeake Bay conforms to this linear relationship. The slope of the regression model indicates that about 24% of organic

matter created or imported to the water column is consumed by aerobic respiration at the sediment-water interface. It is very likely more of the available system carbon is either consumed in sediments (via anaerobic metabolic processes deeper in the sediment column; e.g., Roden and Tuttle (1993)) or buried in the accreting sediment column (e.g., Boynton et al 1995).

While the Nixon (1981) analysis is quite convincing, there was not a direct link developed between water column organic matter production and sediment processes. Deposition of this water column production to the sediment surface was, quite reasonably, inferred but not directly measured. At one site in the mesohaline Chesapeake Bay mainstem vertical arrays of sediment traps were deployed for about a decade, with sampling of trap contents conducted on a weekly to bi-weekly basis (Boynton et al 1993). Thus, at one location, we have a quantitative measure of the amount of organic material reaching the sediment surface. Sediment fluxes were also measured at this site, mainly on a monthly basis, for slightly more than a decade. Results of several deposition - sediment flux analyses are shown in Figure 9-3a and 9-3b. In both analyses deposition rates of total chlorophyll-a (used as an index of labile organic matter) was a strong predictor of sediment ammonium and phosphorus flux. One very interesting aspect of this analysis was the use of lag-times. Deposition rates of total chlorophyll-a were averaged to include early spring deposition of the diatom bloom while sediment fluxes were averaged during the summer period. The detailed reasoning behind the use of lagged variables was presented by Cowan and Boynton (1996). In brief the idea is that deposition of the spring diatom bloom occurred during cool water conditions and this organic material accumulated on the bottom but was not remineralized immediately because of cool temperature. Monthly patterns of surficial sediment PN support this idea. As bottom water temperatures increased in late May, bacterial remineralization increased and summer sediment fluxes of N and P were proportional to the sum of spring and summer deposition rates. This is one of very few data sets we are aware of containing both organic matter deposition rates as well as sediment nutrient fluxes. The major point here is that there appears to be a strong link between organic matter deposition during early spring and summer and the magnitude of summer sediment nutrient fluxes. This, in turn, suggests that the magnitude of sediment nutrient fluxes is a function of nutrient loading rate (and water column production and deposition) for that year rather than a function of organic matter accumulated in sediments during decadal or longer time scales. In short, sediment processes appear to be responsive to changes in external forces, such as nutrient loading rates.

9-3. Time-Series Analyses of Loads versus Sediment Processes

There are several sites in the sediment flux data set where flux measurements were made for a number of years. Sediment flux data from two of these sites (mesohaline sites in the Patuxent and Potomac River estuaries) were organized and examined for relationships with river flow and associated nutrient loads (Fig. 9-4 and 9-5). In both case (i.e., for sediment ammonium and phosphorus releases) significant relationships between inputs and sediment processes were evident. There was considerable unexplained variability associated with these relationships and this was expected because sediment flux is several linkages (algal production, organic matter deposition) removed from river flow and associated nutrient inputs. Sediment fluxes

responded strongly and in a linear fashion to changes in river flows. For example, summer season sediment phosphorus fluxes varied by a factor of three between low and high river flow regimes that also varied by about a factor of three. Ammonium flux and river flow at the Patuxent site varied in a similar fashion but the magnitude of response was by a factor of about two.

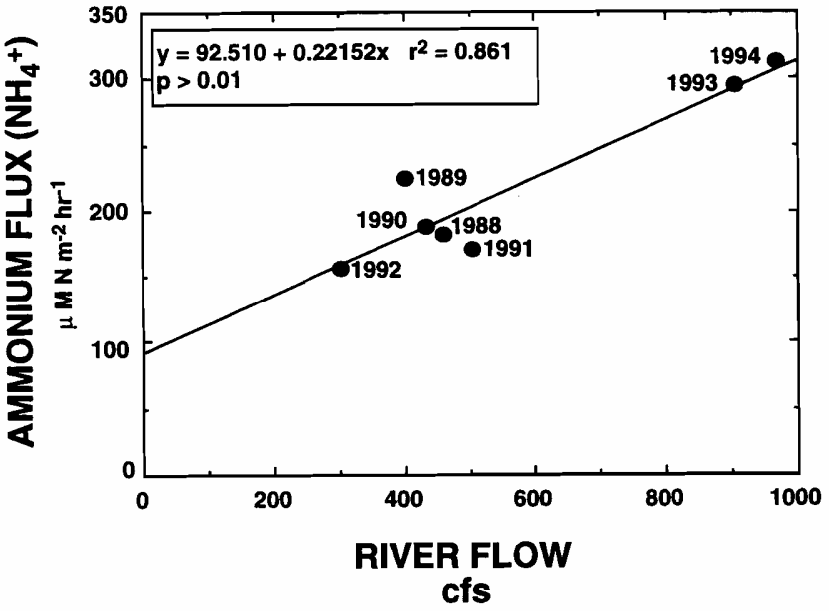

Figure 9-4. *Scatter plots of average monthly river flow and associated nutrients (winter months) versus average summer season ammonium fluxes at a mesohaline site (STLC) in the lower Patuxent estuary. This anaysis was developed by Boynton et al (1992).*

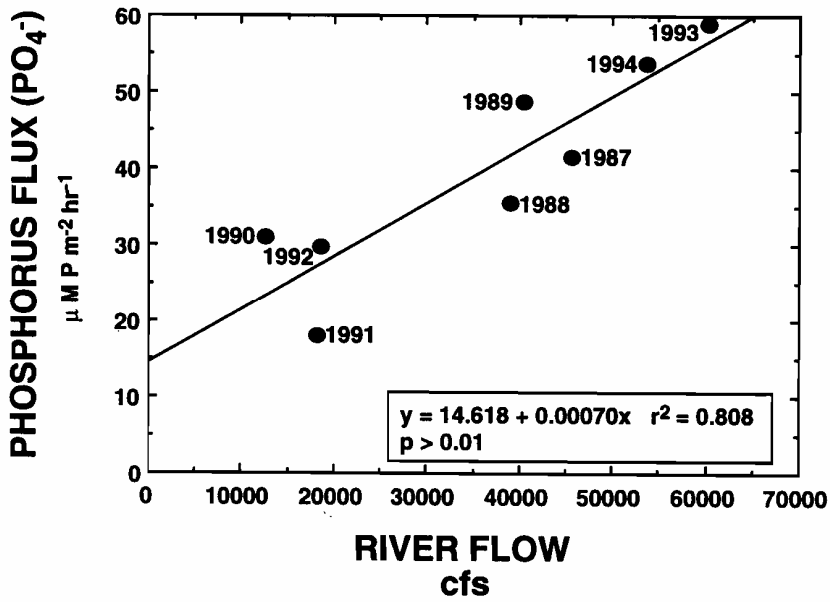

Figure 9-5. *Scatter plots of average monthly river flow and associated nutrients (winter months) versus average summer season phosphorus fluxes at a site (RGPT) in the mesohaline portion of the lower Potomac River estuary. This analysis was developed by Boynton et al (1992).*

9-4. Comparative Analyses of Load versus Sediment Nutrient Flux

We have several analyses, using a comparative rather than time series approach, wherein sediment flux measured from a variety of environments is related directly to nutrient loading rates at these sites rather than to river flow and implied nutrient loading rates during a number of years at a single site. The first of these was developed by Boynton and Kemp (2000) and includes multi-year (4 years) data from four mesohaline sites in different Bay tributaries and the Maryland portion of Chesapeake Bay (Fig. 9-6). Once again there appears to be a reasonably strong relationship to loading rate even using data from sites that span quite a wide water quality gradient. Several points are of particular interest. First, the flux rates from the Choptank River estuary were somewhat higher than

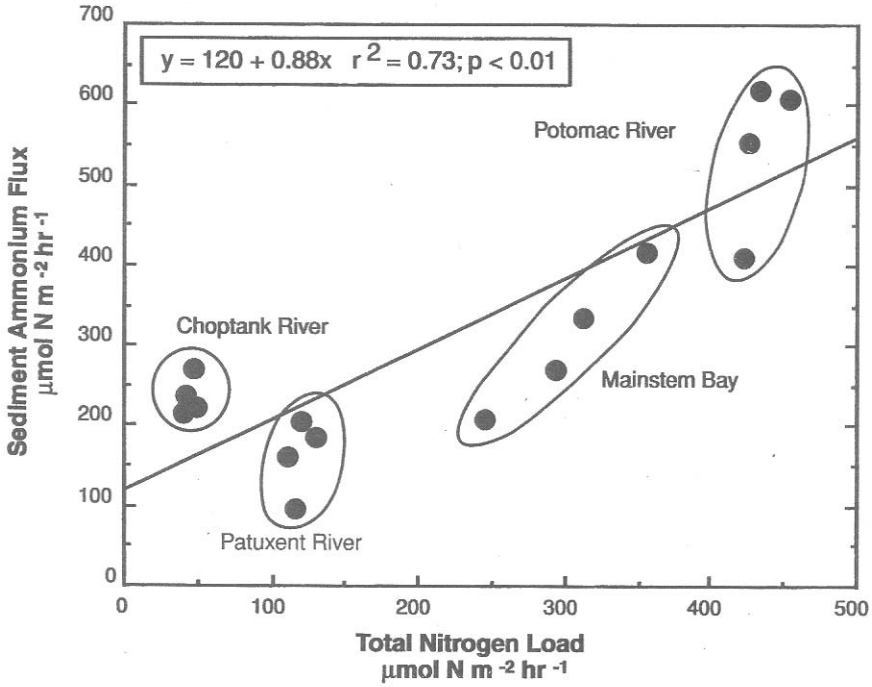

Figure 9-6. *A scatter diagram relating summer (June through September) sediment ammonium flux to average annual total nitrogen load in four locations in Chesapake Bay. Loads and sediment fluxes were measured at the fall line and mesohaline estuarine sites, respectively. Data were from the 1985-1988 period. This analysis was developed by Boynton and Kemp (2000).*

expected. We now have some hints that nutrient loading rates to the Choptank were larger than previously thought (Fisher et al 2006). If this proves to be the case, nutrient load increases would have the effect of moving the Choptank data cluster closer to the rest of the load versus flux relationship. Second, the slope of the load - flux relationship indicates that for every mass unit of load there is about 0.88 mass units of N released from sediments. This indicates that on an aerial basis almost as much N is recycled from sediments each year as comes from external sources, again indicating that sediments are an important cool season repository for labile forms of C, N, and P and an important warm season source of N and P.

Finally, we have organized average summer season ammonium flux data from a number of estuarine sites contained in the sediment flux data base and then developed estimates of winter-spring total nitrogen (TN) loading rates to these systems (Chesapeake Bay Program, Pers Comm.; Boynton et al 1996; Boynton and Kemp 2008). These data

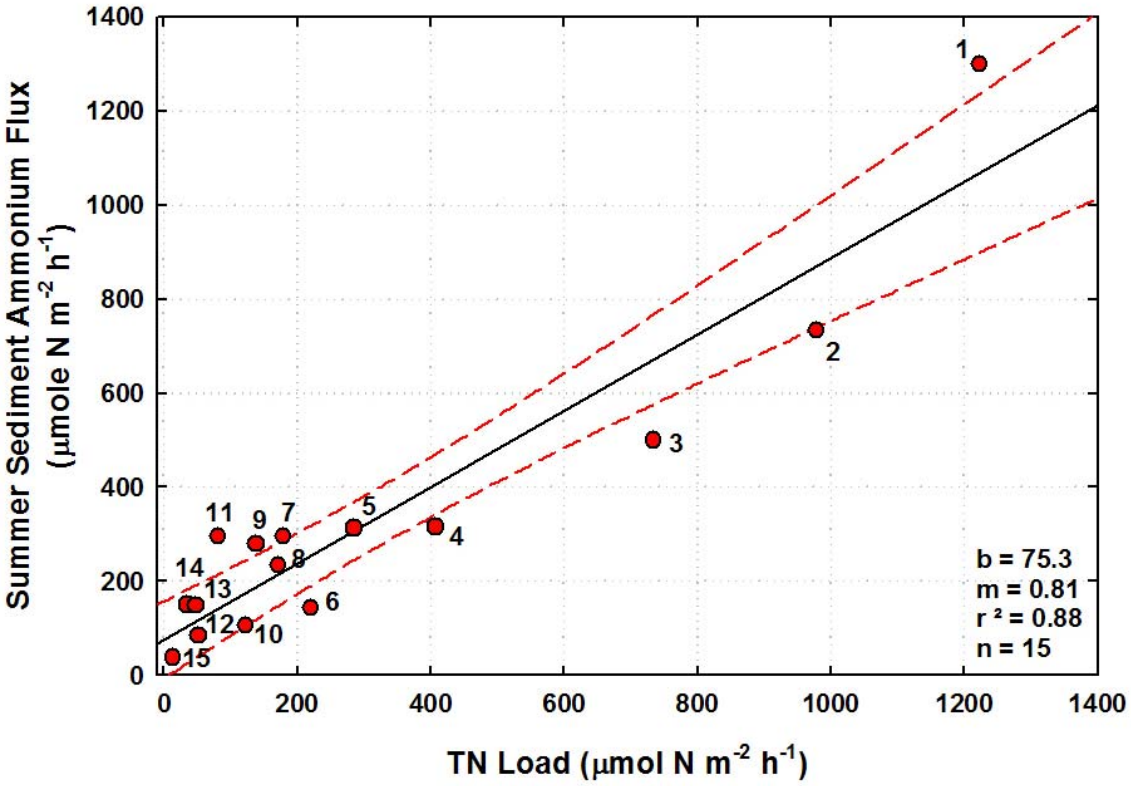

Figure 9-7. *Scatter plot and results of linear regression analysis of total nitrogen (TN) loads versus summer sediment ammonium flux for a selection of Chesapeake Bay tributaries. Sites are coded as follows: 1) Inner Baltimore Harbor, 2) Anacostia River, 3) Back River, 4) Patapsco River, 5) Potomac River, 6) Elk River, 7) Corsica River, 8) Maryland Mainstem Chesapeake Bay, 9) Patuxent River, 10) Sassafras River, 11) Chester River, 12) Assawomen/Isle of Wight Bays, 13) Pocomoke River, 14) Choptank River and 15) Chincoteague Bay.*

are either estimates of sediment flux for a single summer season or an average flux for multiple summer seasons. Loading data were averaged for the year of measurement back to 1985, if data were available from the Chesapeake Bay Program. In this analysis TN loads ranged from about 13 to 1200 µmol N m^{-2} hr^{-1}, almost two orders of magnitude. In the Chesapeake Bay system there is indeed a huge range in loading rates. Summer sediment fluxes also exhibited a large range, from about 38 to 1300 µmol N m^{-2} hr^{-1}. The results of a linear regression analysis of these data reveal several interesting and useful points (Fig. 9-7). First, there appeared to be a strong, near-linear relationship between these variables. About 88% of the variability in summer sediment flux is explained by the average TN loading rate. Despite the fact that loading of "new nitrogen" to these systems is distal from flux, as shown in Figure 9-1, the relationship appears to be quite

strong. In addition, there are both subtle and stronger differences than just nutrient loading rate characteristic of these systems. For example, there are largely tidal freshwater as well as mesohaline sites included. Some sites are vertically well-mixed while others stratified during summer. Finally, as we discussed in Chapter 5, bottom water and sediment conditions also vary widely among these sites. So, we might ask, given these differences among sites, why do we see such a strong relationship between these two processes? One partial answer to this question is that there is a large signal range in these data and 3 of the 15 sites have both very high loading rates and high summer sediment flux. At the lower portion of the data range there is considerably more unexplained variance. However, even if the largest three flux/TN load sites are removed from the data set, there remains a significant relationship. It appears that the coupling between nutrient loading rate, generation of phytoplanktonic biomass, subsequent deposition of this labile organic matter to sediments and recycling of this material as ammonium is very strong. The slope of this relationship suggests that for every one unit of TN delivered to these systems approximately 0.75 units are recycled by sediments, a result very similar to a previous analysis (Fig. 9-6). Thus, sediments provide almost as much nutrient load each year as does the input of new nutrients. In fact, this linkage is likely more interesting than suggested by the load-flux relationship shown in Figure 9-7. In many Chesapeake Bay sites external nutrient loads are much higher in late-winter and early spring than during summer and early fall. Sediment nutrient fluxes are typically very low during winter and early spring. Thus, there is a lag of 4-5 months between peak rates of these two connected processes. During winter spring external loads dominate and act to produce spring plankton blooms. This material deposits to sediments and is temporarily stored there without much decomposition because of low water temperatures. As temperature increases sediment remineralization increases and the original nutrients that entered these systems in winter and spring are returned to the water column throughout the summer, again supplying essential nutrients to support plankton growth, often at excessive levels.

9-5 "Take Home" Summary

- A conceptual model was developed indicating likely linkages between nutrient loading rates and sediment biogeochemical responses. This is an essential step for management since one of the primary goals of the Chesapeake Bay Program is to reduce nutrient loading rates to the Bay system. This model and subsequent analyses indicate that sediment fluxes should track nutrient loading rates.
- Multiple analyses indicate links to sediment processes from distal (inputs) and more proximal (plankton production, organic matter deposition rates) causative factors, again as suggested by the conceptual model.
- There are strong indications that the magnitude and pattern of sediment processes respond to causative factors on annual rather than longer time scales. This suggests responsive sediment process rather than processes that have longer time constants.
- Both time-series and comparative analyses suggest strong coupling to nutrient loading rates and the sequence of cause-effect relationships suggested in the conceptual model.

- Comparisons of nutrient loads from external sources (e.g., diffuse and point sources) to sediment nutrient releases indicate they are about equal in magnitude. Thus, if just these two processes are considered, the load from the land is doubled because sediments recycle an amount of N about equal to the annual load from external sources.

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Chapter 10

Sediment Nutrient Memory

10-1. Issue of Estuarine Nutrient Memory

An important issue for water quality managers and estuarine water quality modelers concerns the likely water quality (and associated habitat) response times to changes in a variety of input variables (e.g., river flow, nutrient loads). For example, if nitrogen loads to the mainstem Chesapeake Bay were to decrease by a large amount (~2X) in response to major management actions, how long would it take for water quality conditions in the Bay to change? Or, if there was a prolonged period of drought conditions, with low freshwater and nutrient input, what would the water quality response time be?

Our impression is that many in the research and management community believe that there is a very large store of C, N and P in estuarine sediments, accumulated there during the last four or five decades when the estuary was very eutrophic. Based on those observations many have concluded that water quality responses to management actions will be muted because of this large nutrient and organic matter storage. While it is clear that indeed most of the C, N and P stock is in the sediment pool we will argue that a very large fraction is either not very reactive or is not biologically available. The end result is that these estuaries have a relatively short "nutrient memory" and should respond rapidly (seasons to year time scale) to changes in loads. We base these arguments on examination of water quality variables as well as sediment processes, natural field experiments embedded in these time series measurements and laboratory experiments involving manipulated sediment cores. We also provide an example from the Patuxent River estuary indicating just how much of the system N and P are contained in the sediment pool.

10-2. Major Storages of N and P

Boynton et al (2008) recently completed a nutrient budget for the Patuxent River estuary, a moderately eutrophic tributary of Chesapeake Bay. As a part of this budget four N and P storages in the estuary were evaluated, including water column dissolved and particulate nutrient stocks, macrobenthic invertebrate and zooplankton biomass and surficial sediment stocks. A brief synopsis of results is provided here. They found that at the whole-estuary scale the annual average total mass of TN in the water column was about 550 x 10^3 kg N. At the whole-estuary scale the total mass of TP in the water column was about 42 x 10^3 kg P. Macrobenthic N and P biomass was 119 x 10^3 kg N and 5 x 10^3 kg P, representing 4.4% and 0.7% of the N and P in the system. Annual annual N and P biomass in zooplankton was even smaller, amounting to 4.9 x 10^3 kg N and 0.83 x 10^3 kg P, or about 0.2 and 0.1% of the total N and P stock, respectively. Most of the N, and even more of the P, in this system were contained in the sediments. Somewhat arbitrarily, only the upper 2 cm of the sediment column was used in this analysis, so as to include only the N and P that was deposited relatively recently and still potentially available to ecological processes. About 75% of TN and about 93% of TP in the system were in sediments. We suspect that other tributaries of the Bay follow a similar partitioning of N and P with the deeper systems having somewhat more N and P

in the water column. In any case, the point is clear that N and P storages are primarily in the sediments and this is where "nutrient memory" would reside.

It is interesting to note that most of the N and P in the Patuxent is detrital organic matter (in the case of N) and particulate inorganic material (in the case of P). A very small fraction is in living biota. It seems likely that the fraction contained in living biota was once much higher for several reasons. First, it appears that benthic infaunal biomass has been substantially reduced from historically higher levels (D'Elia et al 2003). Compared to benthic biomass estimates assembled by Herman et al. (1999), Patuxent values were 2 to 3 times lower than those observed at similar levels of primary production in other estuarine systems not having chronic hypoxia problems. Second, Stankelis et al. (2003) assembled data concerning seagrass communities in the Patuxent from the late 1930s to the present. Seagrasses were once a large feature of the Patuxent and represented a substantial storage of nutrients in living tissue. Old records from the Academy of Natural Sciences of Philadelphia (1965-1975) also indicated that epiphytic and benthic diatoms were a significant feature of the Patuxent, but these autotrophs have largely been lost in recent decades. The status of fish stocks, both commercial and forage, is far less clear, although long-term residents uniformly insist that fish were far more abundant prior to the 1970s. These observations suggest that the partitioning of N favored living, as opposed to detrital, storages prior to the estuary becoming eutrophic. If any of this is true, these longer-lived N storages would represent a nutrient buffer, restricting nutrient recycling to rates below those associated with very rapid bacterial remineralization of labile substrates (i.e., phytoplanktonic debris) observed under present conditions. These simple observations may generally apply to other regions of the Bay as well and may be more pronounced in the shallower tributaries.

Thus, it seems clear that most of the N and P in these systems is in sediments and therefore represents a potential internal source or memory. In the next sections we examine primarily sediment flux data to see if there is evidence for multi-year nutrient memory in these estuaries.

10-3. Evidence for Short Nutrient Memory

There are three lines of evidence indicating the sediment nutrient memory is relatively short, likely on the scale of seasons to several years rather than decades. The first line of evidence comes from examining Bay responses to major environmental events (major floods and multi-decade increases in nutrient loading rates). The second is based on examination of sediment nutrient flux time series data from a few locations in the Bay system. The third is based on experimental sediment flux work where the focus of the experiments were to examine the time for sediments to exhaust internal supplies of organic matter and nutrients. In all cases the end results suggest a limited sediment-based nutrient memory.

10-4..Large Event Effects

On rare occasions weather events can cause large disturbances to the Bay system. One such notable event occurred during late June, 1972 when tropical storm Agnes stalled over the Susquehanna River watershed and, as a result, huge amounts of water, sediments, organic matter and nutrients were discharged into Chesapeake Bay (see Chesapeake Research Consortium 1976). Monthly Susquehanna River flow for the

period 1968 - 1977 exhibited clear intra-annual patterns with highest flows usually associated with the winter and early spring (Fig. 10-1). However, flows were especially high during June, 1972, the highest June flow on record. This flood delivered large

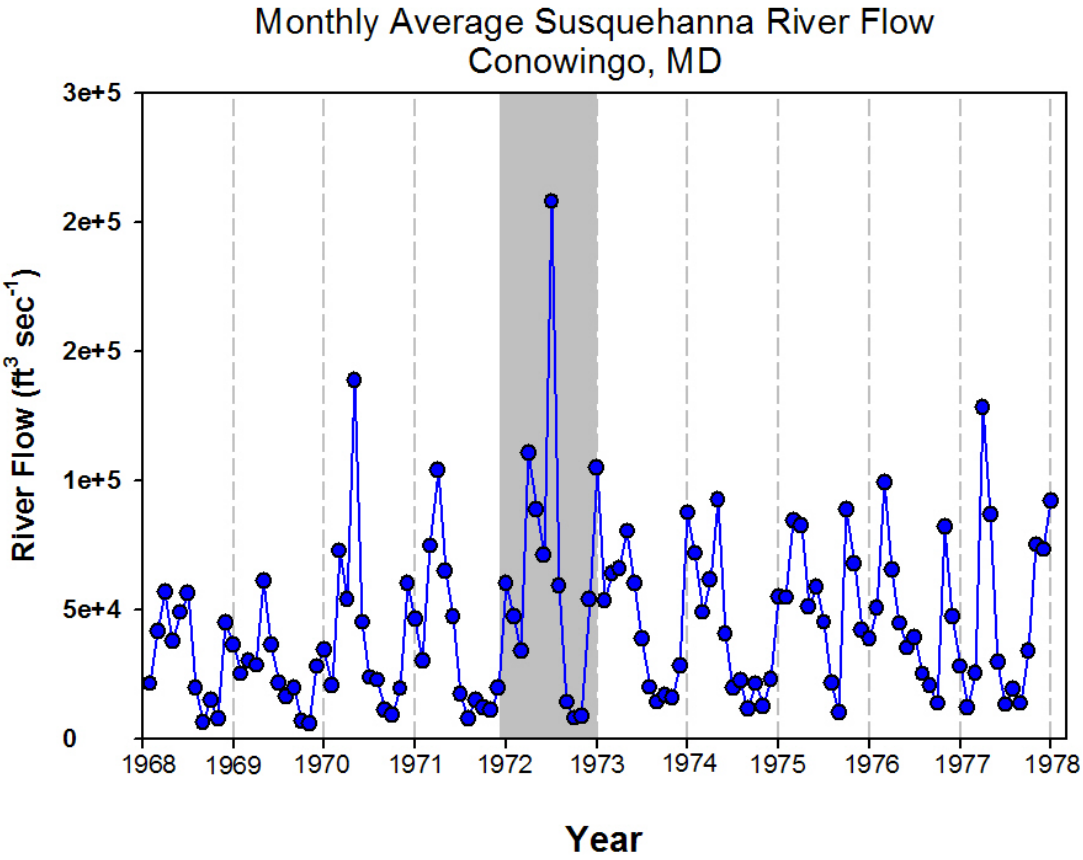

Figure 10-1. *Monthly average flows (cfs) from the Susquehanna River for the period 1968-1978. Data are from USGS (http://waterdata.usgs.gov). The year Tropical Storm Agnes occurred is shaded.*

amounts of N and P to the estuary at a time when summer phytoplankton communities were beginning to develop. Following 1972, flows exhibited expected patterns and magnitude through 1977. A few months prior to the storm, Mihursky et al (1977) began making routine measurements of water quality, algal biomass and primary production rates at six locations in the mesohaline Bay. These measurements were made on a monthly basis and continured through 1977 (Fig. 10-2) and additional measurements were made by the Chesapeake Bay Program from 1985-1993. The essential point from this analysis was that there was an immediate response in algal biomass and production to increased river flow (a good index of nutrient loading rate in this case). In 1973 river flow returned to normal but algal biomass and production was much higher relative to nutrient loading rates for 1973. Hence, there seems to be a nutrient memory related to this massive flood event. However, the signal in the plankton community soon faded and rates and concentrations returned to normal ranges by summer 1974. Excellent relationships between river flow (i.e. nutrient loading) and algal responses are evident when a one year lag is added to regression models of flow versus algal production (Fig. 10-3a) and algal biomass (10-3b). A massive event like Tropical Storm Agnes seems to

have left a temporal signal lasting about 2 years. This analysis suggests a limited storage of either nutrients or labile organic matter in the system.

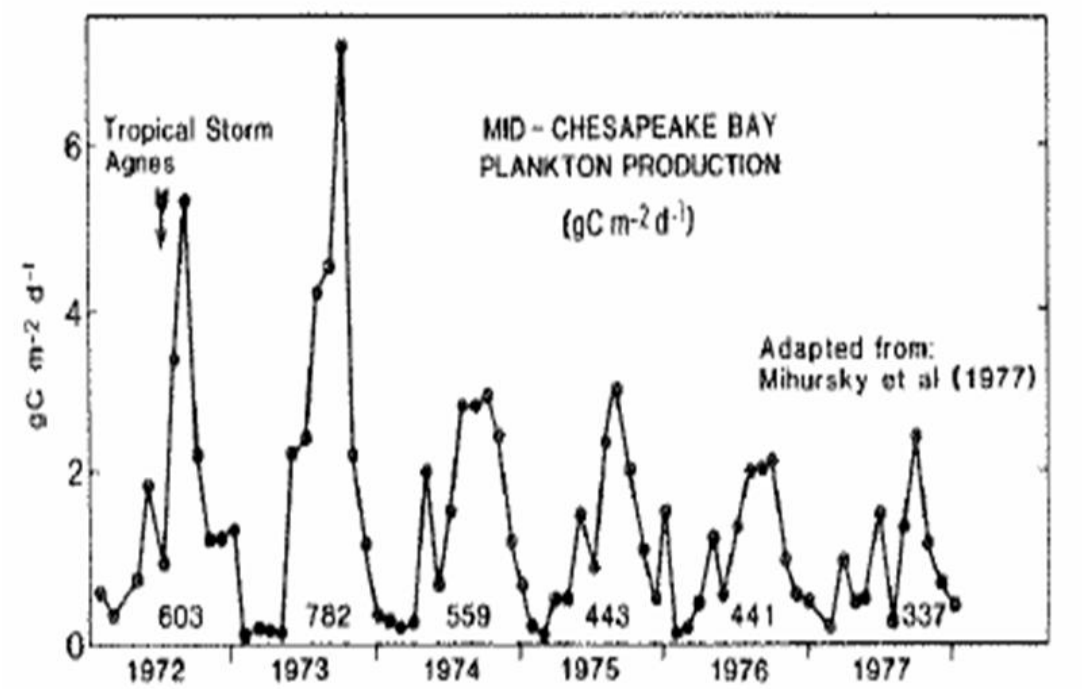

Figure 10-2*. Monthly average phytoplankton production rates for a series of 6 stations in the mesohaline portion of the Chesapeake Bay. Data were collected by Mihursky et al. (1977). Data for 1985-1993 (not shown) were also available from the Chesapeake Bay Program.*

In a more detailed fashion, Harding and Perry (1997) reconstructed algal biomass patterns for the mainstem Bay. While they discussed many aspects of this time-series, the most relevant here is that algal biomass increased from about 1950 to 2000 in step with increases in nutrient loading rates. Interestingly enough, the reduced loads occurring during the mid-1960s drought are reflected in reduced and redistributed algal biomass in the Bay. If there was a large storage of nutrients (or organic matter-bound nutrients) we would not expect rapid and clear responses from the plankton community.

10-5. Sediment Flux Time-Series

We have made the argument earlier that sediments are the likely place where nutrients, organic matter or other materials can potentially be stored on an inter-annual basis. If there were large reserves of nutrients in estuarine sediments then we would expect seasonal sediment fluxes to be closely related to water temperature (see Chapter 6) and not particularly responsive to inter-annual variations in inputs of new nutrients from the basin. However, we have already shown that there are strong indications that sediment fluxes appear to be limited, even within a summer season, by the availability of labile organic matter. We have pursued this matter of sediment responses to inter-annual variations in nutrient load (in this case nutrient loads generate planktonic organic matter and this material sinks to sediments thereby providing labile material to support sediment biogeochemical processes) at a number of Bay locations where sediment flux time-series

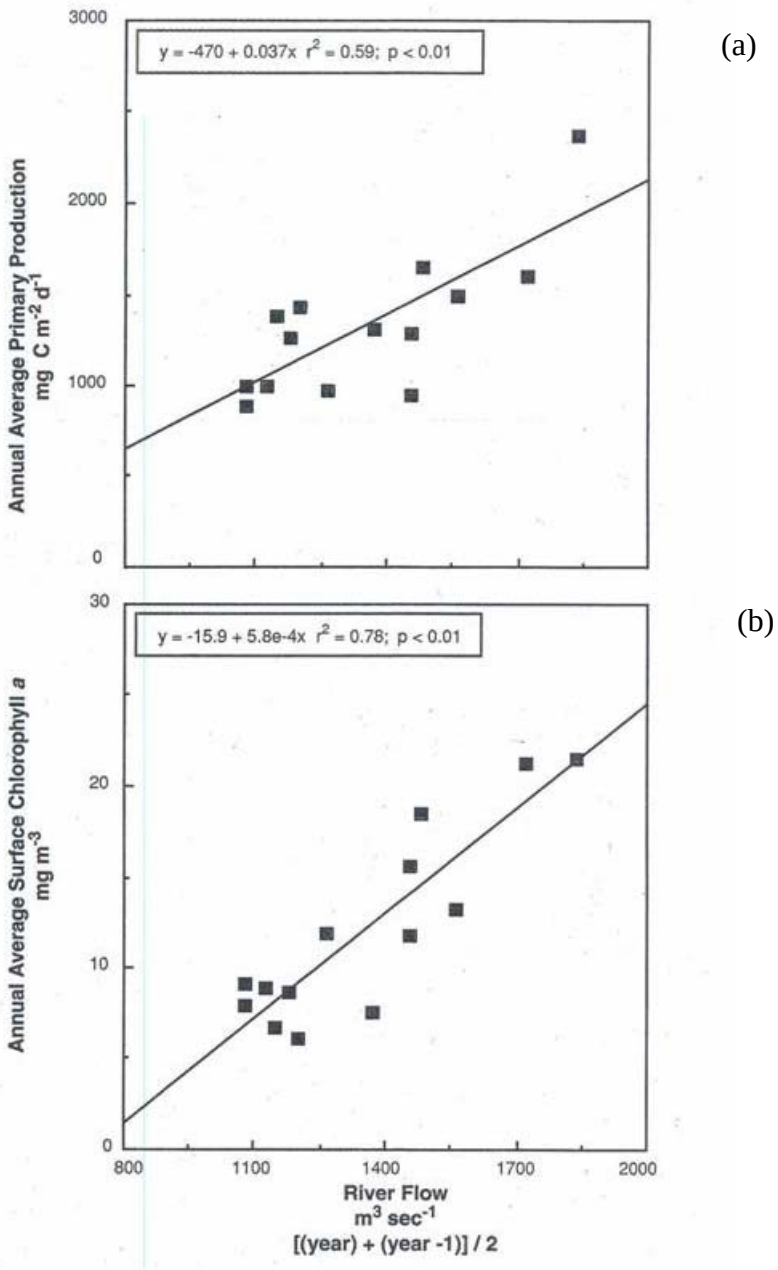

Figure 10-3. *Results of regression models showing relationships between annual average primary production (a) and surface chlorophyll-a (b) and freshwater flow from the Susquehanna River. River flow was calculated as the average flow in the present and preceding year. Data from Mihursky et al. (1977) and Chesapeake Bay Program (1985-1993).*

data are available. One such example is provided in Figure 10-4 for a site in the mainstem Bay. In this case there is a factor of about 2.5 increase in sediment ammonium flux for a similar increase in river flow. Similar results have been noted for locations in the Patuxent River and for a comparative analysis of these and other sites reported by Boynton and Kemp (2000). The point here is these sediment processes appear to be

responsive to loading rates. If internal stores were large, we would not expect such strong and consistent relationships to inputs of new nutrients (and the organic matter produced by those nutrients) and ammonium being recycled from sediments.

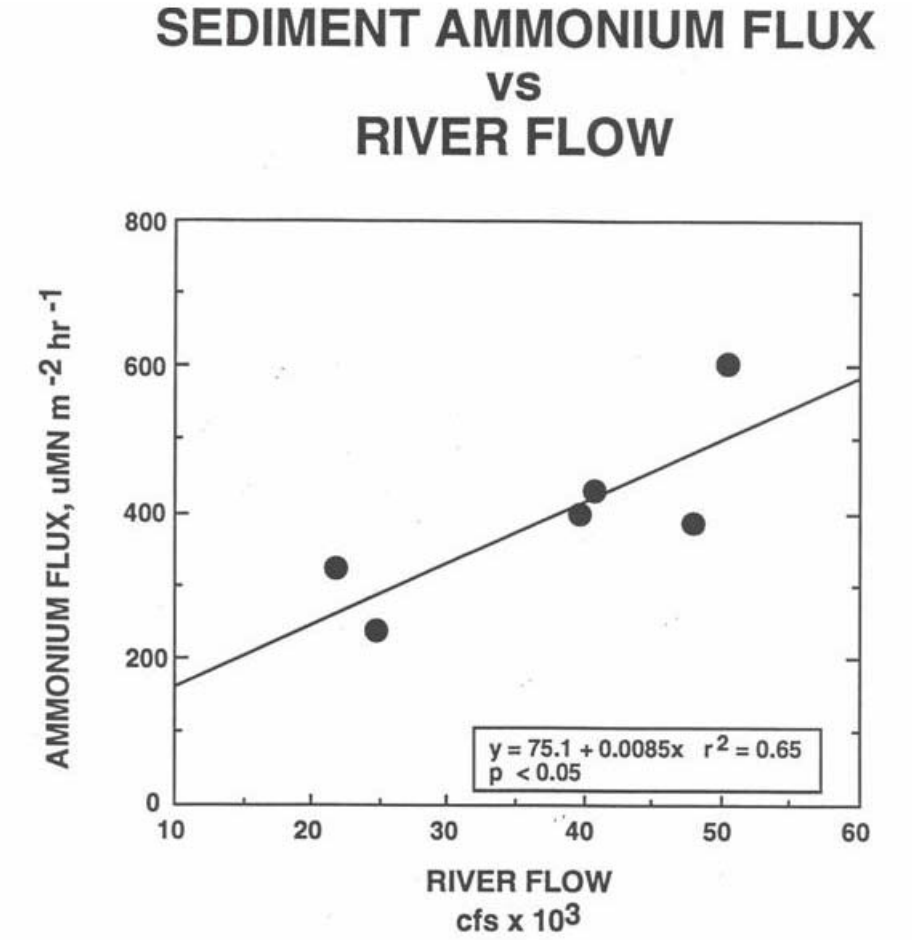

Figure 10-4. *Results of a linear regression analysis of average annual river flow versus summer sediment ammonium flux. River flow is from the Susquehanna River and sediment ammonium fluxes from a station in the mesohaline Bay (station R-64).*

10-6. Experimental Studies

While much can be learned from inspection and analysis of time-series data there are limitations to this method. For example, there is no control over the degree to which inter-annual loadings vary. Warmer and cooler water may be associated with lower and higher loading rates and thus add additional complexity to an analysis. In short, while field studies have great realism they suffer from lack of strong controllability. Because of this we have also conducted a series of sediment flux studies by bringing sediment cores (to maintain realism) into a laboratory setting (for controllability) and conducted a series of experiments designed to explore the degree to which ambient fluxes can be maintained without addition of new labile organic matter. In effect, these experiments were testing the "nutrient or organic matter memory" of sediments. Three related experiments were conducted with one focusing on SOC rates (Fig. 10-5a) one on

anaerobic metabolism (Fig. 10-5b) and one a sediment P flux conducted under continuous normoxic and near-anaerobic conditions (Fig. 10-6). In all experiments sediment cores were maintained at ambient Bay summer temperature and salinity. Water overlying the sediments in the cores was continually exchanged with ambient water to maintain realistic nutrient concentrations and concentration gradients. However,

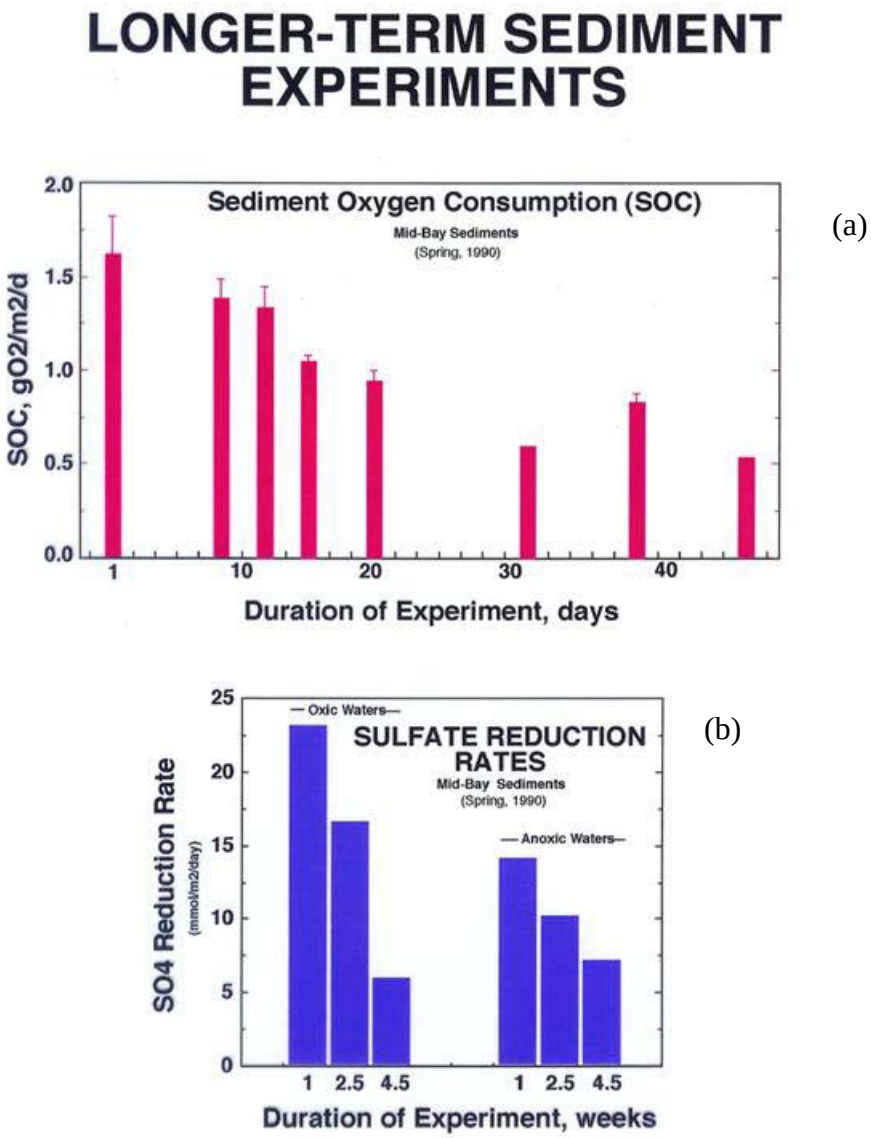

Figure 10-5. *Time series of sediment SOC (a) and sulfate reduction rates measured under laboratory conditions (T ~ 25 °C; salinity ~ 15). Cores were collected after deposition of the spring bloom in the mesohaline mainstem Bay (station R-64). Ambient water was regularly exchanged in the cores, but all particulate organic matter was removed via pre-filtration.*

replacement water was filtered to remove all particulate organic matter. Essentially, these cores were being starved and the point was to observe how long ambient rates could be maintained. The overall result of these experiments was that sediments were very

responsive to changed conditions. In the case of SOC and anaerobic metabolism experiments (Fig. 10-5 a and b) rates decreased rapidly when new organic matter supplies were terminated; SOC rates declined by a factor of 3 in about 30 days and sulfate reduction rates (with and without oxygen in overlying waters) decreased by even larger margins. Both of these experimental results are consistent with field observations. In the phosphorus experiment sediment P fluxes increased rapidly after being exposed to near-anoxic conditions and fluxes reached magnitudes observed under field conditions after just 4.5 days of exposure. However, these rates were not maintained. Rather, fluxes steadily decreased and after 20 days were only 25% of maximum rates. These results again suggest a limited nutrient memory and a memory, less than seasonal time-scales.

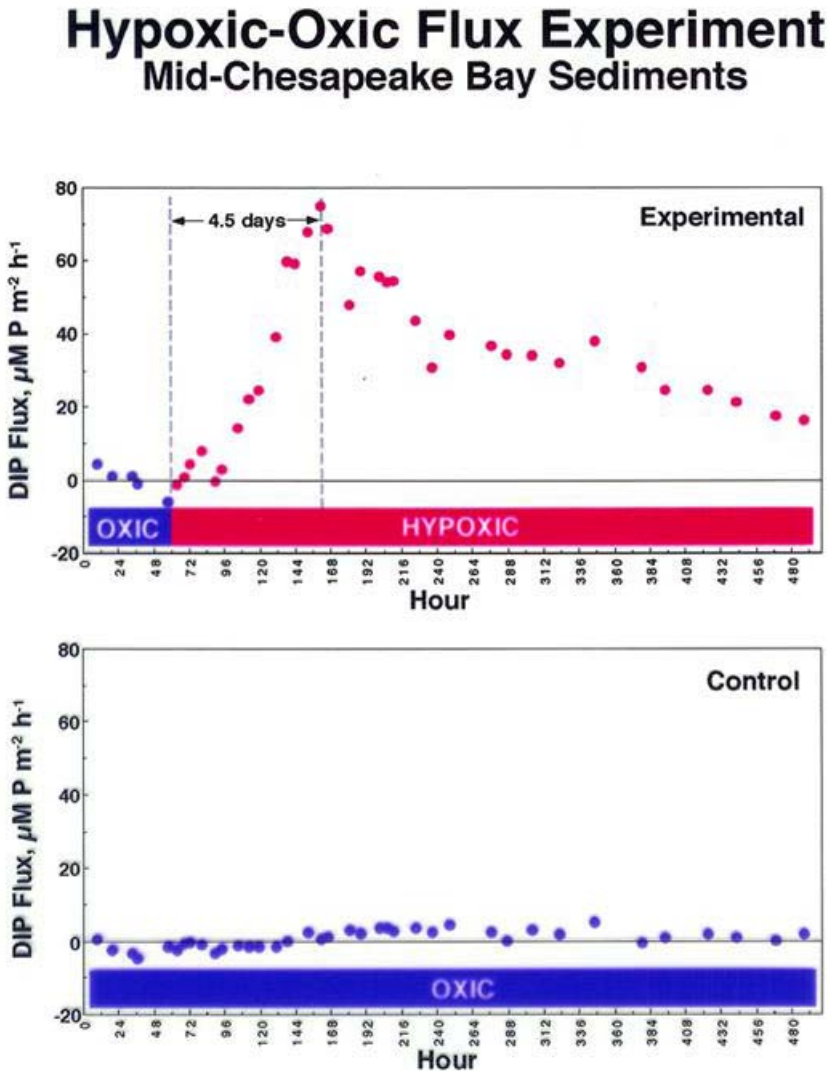

Figure 10-6*. Sediment phosphate flux in sediment cores exposed to hypoxic / anoxic overlying waters (top panel) and to normoxic overlying waters.*

10-7. "Take Home" Summary

- Examination of estuarine nutrient storages indicate that most of the N and P in these systems are contained in bottom sediments. If there is a reactive nutrient storage (nutrient memory) then it is clearly located in the bottom sediments.
- It is often assumed that there is a long nutrient memory in these shallow estuarine systems because nutrients loads have been elevated for 4-5 decades and longer in some cases. The management implication of this is that these systems will not rapidly respond to nutrient load reductions.
- Examination of both water column and sediment flux time series data and laboratory experimental data suggest that sediment fluxes are maintained by very recent delivery of labile organic matter. Sediment fluxes appear to respond to changes in organic matter supply rates on time scale of weeks to months rather than years to decades. If large changes in nutrient loads occur we would predict rapid changes in sediment oxygen and nutrient fluxes and rapid improvement in water quality
- Water quality models need to have sediment flux components that are responsive to changes in labile organic delivery rates to sediments. Models that have non-responsive sediment components are probably not accurate and should be replaced.

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Chapter 11

Sediment Nitrogen Processes and DO Conditions

11-1. Background

Previous chapters of this report have made the general importance of bottom water DO conditions on water quality, habitat quality and sediment biogeochemical processes obvious. The conceptual model depicting estuarine degradation and restoration trajectories invokes DO conditions in several places (Fig. 1-1). We have again displayed the conceptual model in this chapter to make reference to this diagram easier (Fig. 11-1).

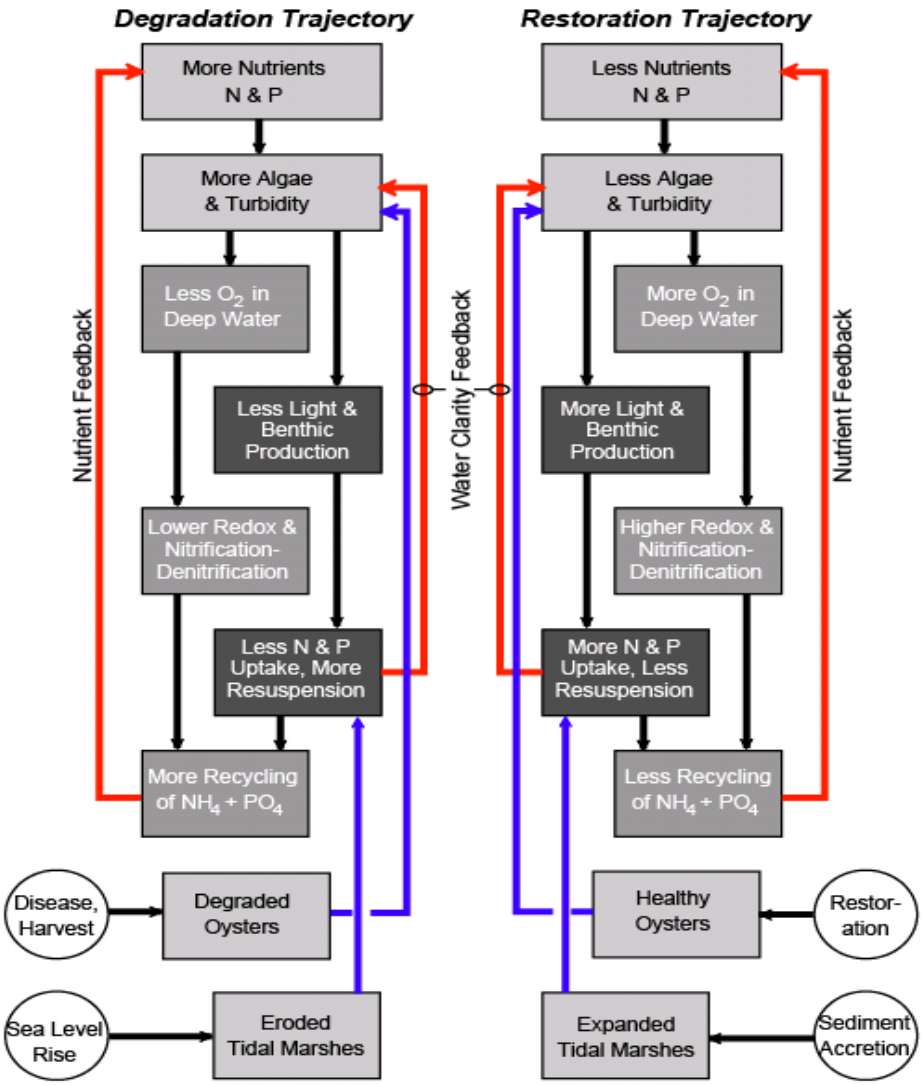

Figure 11-1. *A conceptual model (presented in Chapter 1) of nutrient induced eutrophication for estuaries such as Chesapeake Bay. Note that there are both degradation and restoration trajectories. Of particular importance here are the positive feedbacks induced by low oxygen conditions on sediment-water nutrient processes. This diagram was developed by Kemp et al 2005.*

Specifically, the conceptual model indicates that nutrient loads promote algal growth and increases in water column turbidity. This, in turn, leads to lower DO concentrations in deep waters and diel-scale hypoxia in shallower areas. These low DO conditions have profound impacts on sediment biogeochemical processes. In particular, when DO concentrations decline, sediment nitrification (production of nitrate from ammonium) also declines as does the coupling of this process to denitrification. Thus, of the organic N that reaches sediments, most is simply returned to the water column as ammonium and this recycled N supports continued high plankton production and reinforces low DO conditions. The restoration trajectory follows, at least as indicated in Figure 11-1, the reverse direction. However, these systems have non-linear properties (see Kemp et al 2005) and sediment, or other ecosystem properties, may not follow simple pathways to a restored state. In this section we will use the sediment flux data set and information from other estuarine systems to examine the influence of bottom water DO conditions on sediment nitrogen fluxes.

11-2. Bottom Water DO and Eh Conditions

There are a number of conditions that lead to low DO conditions in estuaries. Included among them are water column depth, degree of water column stratification, supply rate of organic matter from the upper euphotic layer of the water column to deeper

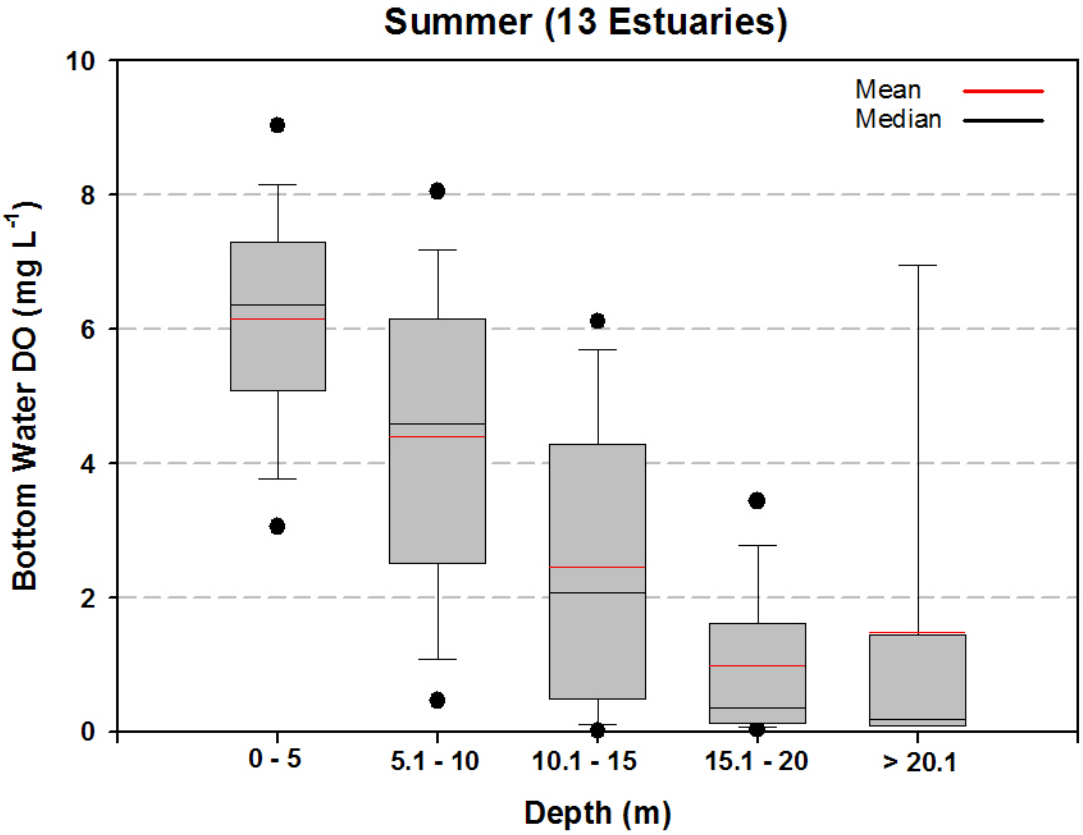

Figure 11-2. *Box and Whisker plots of bottom water DO concentrations as a function of water depth during summer periods from 13 tributaries in the sediment flux database.*

waters and the flushing time of the waters in question. Many of these factors interact as well in regulating DO conditions.

In the flux data set there is a very large range in DO conditions at the sediment-water interface. Dissolved oxygen concentrations range from near-anoxic to almost super-saturated. Hence, we have a good opportunity to examine DO effects on sediment N fluxes.

One general trend in bottom water DO concentrations during summer periods is that concentrations decrease with depth (Fig. 11-2). At most shallow sites (< 5 m) DO concentrations are close to saturation at summer temperature conditions. However, at stations >5 m but < 10 m median DO concentration is just over 4 mg l^{-1} and at sites greater than 10 m median concentrations are < 2 mg l^{-1}. These DO measurements are collected about 1 m above the bottom so DO conditions at the sediment-water interface are very likely lower than those reported here. Sediment Eh conditions show a similar relationship to depth (Fig. 11-3). The likely explanation for these depth related patterns is that bottom water at deep sites has less opportunity to be re-aerated via mixing processes.

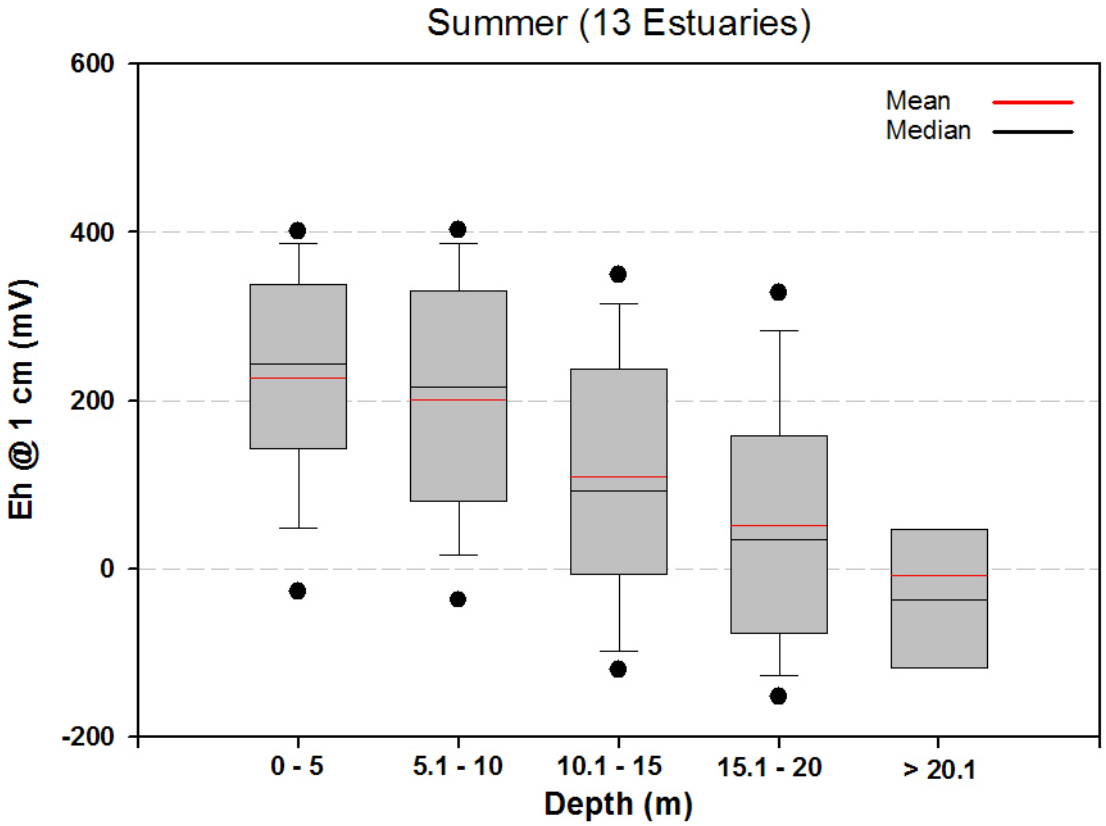

Figure 11-3. *Box and Whisker plots of sediment Eh as a function of water depth. Data are for summer periods from 13 tributaries in the sediment flux database.*

At deep and strongly stratified sites, mixing is very small and hence DO supply from the atmosphere very restricted. The similar pattern in Eh measurements indicates that sediments at deeper sites have been chronically exposed to depressed DO conditions. One method of examining sediment N flux related to DO conditions is to compute the

ratio of DO used by sediments to the amount of ammonium released by sediments, ammonium being the initial inorganic N compound produced during remineralization.

11-3. Sediment O:N Flux Ratios

In Chapter 5 the basis, computation and utility of O:N flux ratios was explained in detail. In brief, phytoplankton are the major source of organic matter to sediments in almost all regions of Chesapeake Bay (Kemp et al 198? C budget paper). Phytoplankters have a nominal composition of major constitutents (C, N, P) of 106:16:1 (on an atomic basis). So, as this material is decomposed we would expect that for every 106 atoms of C remineralized to CO_2, about 16 atoms of N would be released as ammonium. If we compute the amount of oxygen needed for this decomposition we find that about 13 atoms of oxygen (computed as O rather than O_2) would be consumed for every atom of N produced as ammonium. Thus, we can use the sediment flux of oxygen and ammonium to see if simple remineralization is occurring (generating O:N flux ratios of about 13) or if some other processes are causing this ratio to be either larger (N is being preferentially lost relative oxygen consumed) or smaller (some other source of N is involved, possibly from anaerobic metabolism of organic matter deeper in the sediment column.

In Chapter 5 O:N flux ratios were described for 13 sub-systems of the mainstem Bay and tributary rivers. Two tributaries were selected to more closely examine sediment O:N flux ratios and these systems (Chester and Patuxent River estuaries) also exhibited different distributions of bottom water DO conditions and water depth. Sediment O:N flux ratios at sites located along the axis of the Chester River estuary were generally elevated and ranged from about 19 to 85, with most ratios being between 20 and 60 (Fig. 11-4). One site at the mouth of the Chester had an O:N flux ratio less than 13 and, interestingly enough, bottom water DO conditions at that site were depressed, the only site where that was the case. Flux ratios greater than 13 indicate that some N is missing relative to that expected from decomposition of phytoplanktonic organic matter. The Chester is relatively shallow and DO conditions at all but one site were relatively high during the summer period when these measurements were collected. Thus, SOC rates were not likely to be limited by low DO conditions. In the Chester River it is likely, because of adequate DO in bottom waters, that ammonium generated by decomposition processes in sediments was then nitrified (an obligate aerobic process) and then denitrified (in anaerobic sediments), minimizing the amount of N recycled back to the water column. In addition, in the lower Chester River nitrate was observed leaving sediments, a certain sign that nitrification was taking place. Thus, the Chester is a place where adequate bottom water DO conditions (partly promoted by shallow water depths and a well mixed water column) supported sediment processes that tend to rid the system of excessive N.

In contrast, O:N flux ratios in the Patuxent exhibited two distinctly different patterns and these patterns appeared to be related to depth and bottom water DO conditions (Fig. 11-5). At three shallow sites (depths <4 m) sediment O:N flux ratios were elevated (75 to 180), and bottom water DO concentrations were relatively high. These sites were similar to those in the Chester having high bottom water DO conditions, shallow depths and high sediment O:N flux ratios. However, at deeper (>5 m) sites DO concentrations were quite low (< 4.5 mg l^{-1}) and sediment O:N flux ratios were close to or about 13, the ratio expected for simple recycling of N from decomposing

phytoplanktonic organic matter. In this case, there appears to be no operational N shunt to denitrification (via sediment nitrification) that would tend to stabilize N dynamics in this estuary. The situation at deeper Patuxent River sites appears to be following the degradation pathway indicated in Figure 11-1.

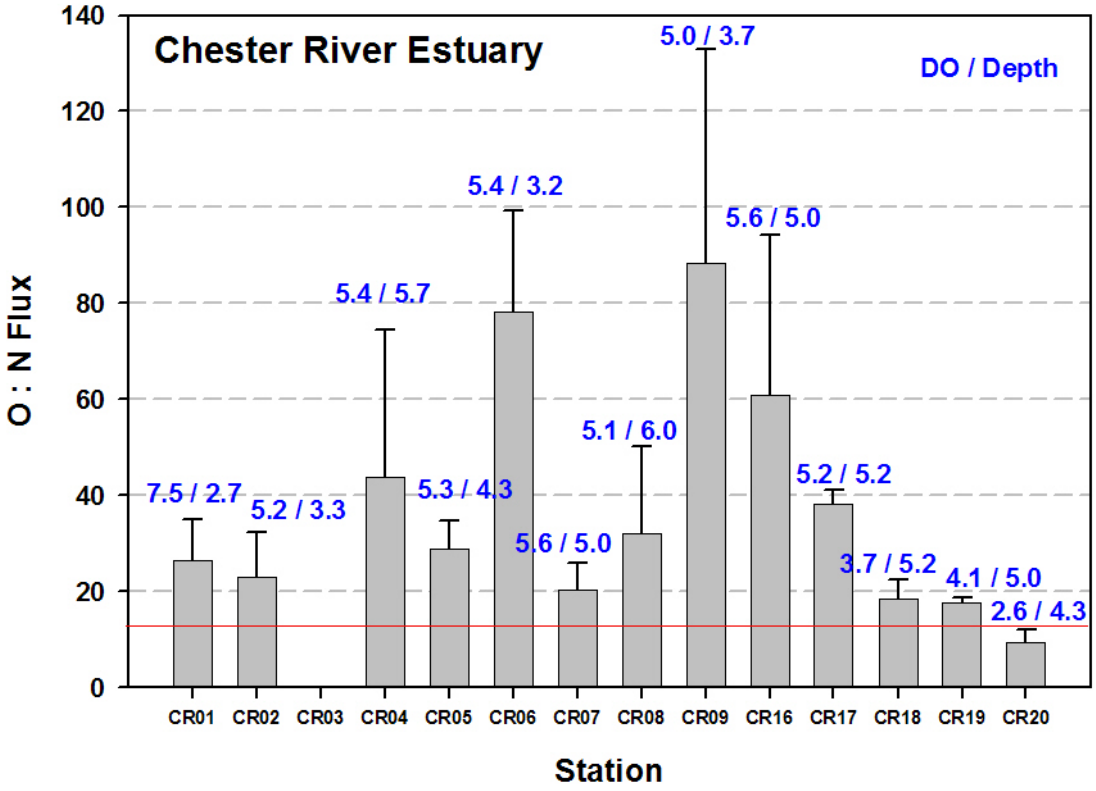

Figure 11-4. *Bar graph of sediment O:N flux ratios (June-August data) along the axis of the Chester River estuary. Numbers above each bar represent bottom water DO concentration (mg L^{-1}) and water depth (m) respectively.*

Unfortunately, we are speculating about the occurrence of coupled nitrification-denitrification at most of Chesapeake Bay sediment flux sites. Our arguments are consistent with coupled nitrification-denitrification either being operative or not but we have few direct measurements to support this assertion. However, in theory and practice, coupled nitrification-denitrification represent one of the "self-healing" mechanisms that, if activated, would greatly assist in restoring water quality conditions. It seems, as we will show more clearly in the next section, that increasing DO concentrations in bottom waters will allow this negative feed-back process to operate.

11-4. Sediment Denitrification and Nutrient Recycling Efficiency

We do have some measurements of denitrification that are particularly relevant to the issue of sediment N recycling and bottom water DO conditions. Here we present some background information on estuarine denitrification rates and controls and then present an analysis that lends support to the conclusions presented in the previous section.

Denitrification, which represents an important process for removing fixed N from estuaries, occurs in the upper stratum of sediments where rates tend to be limited by

availability of nitrate. Nitrate is also produced via nitrification near the sediment surface which is, in turn, limited by availability of DO. A recent review of denitrification rates in aquatic systems included 1757 measurements from 152 sites during a 45 year period (Greene 2005). Most reported denitrification measurements indicated rates between 11 and 100 µmol N m^{-2} h^{-1}, with few rates < 1 µmol N m^{-2} h^{-1} and few in excess

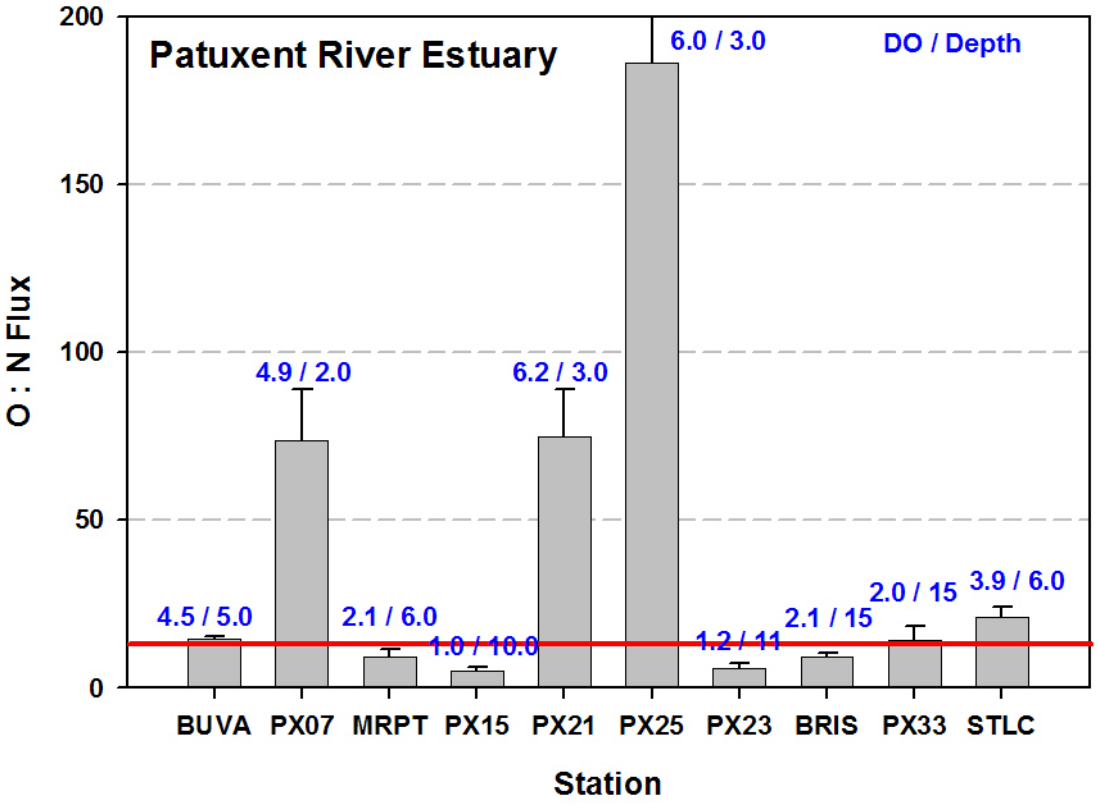

Figure 11-5. *Bar graph of sediment O:N flux ratios (June-August data) along the axis of the Patuxent River estuary. Numbers above each bar represent bottom water DO concentration (mg L^{-1}) and water depth (m) respectively*

of 1000 µmol N m^{-2} h^{-1}. In estuarine systems the most commonly reported rates were between 1 and 50 µmol N m^{-2} h^{-1}, but almost 40% of measurements were larger. Estuaries were also the most intensively measured systems (56 % of all measurements), although many estimates were also available for continental shelves, coastal wetlands, lakes, lagoons, inland wetlands and several other environments. Mean rates in most systems were between 50 and 250 µmol N m^{-2} h^{-1}. It is useful to note that denitrification rates of 200 µmol N m^{-2} hr^{-1} are equal to about 25 g N m^{-2} yr^{-1}, a substantial fraction of TN loading rates to many estuaries, including some of the nutrient-impacted tributaries of Chesapeake Bay.

Several earlier papers helped place denitrification, as an internal loss term, into the context of the N economy of estuaries. Seitzinger (1988) summarized available data from lakes, rivers and estuaries regarding the ecological significance of this process. Important conclusions were that denitrification rates were higher in systems receiving large, anthropogenic nutrient inputs, most of the NO_3 consumed in denitrification

apparently came from sediment-based nitrification rather than from the water column and, from a small sampling of estuaries, denitrification rates were proportional to TN loading rates, removing an average of 40% of N inputs. More recently, Nixon et al (1996) computed the proportion of input N removed via denitrification from a larger selection of estuaries and several lakes, with values ranging from 10 to 74%, again indicating the importance of this process. It is very instructive to note that Chesapeake Bay systems appear to remove less N than expected from the Seitzinger (1988) and Nixon et al (1996) analyses. Boynton et al (1995) reported that about 25% of TN entering the mainstem Bay and Potomac River estuaries was denitrified. At this point, the most likely explanation for this reduction in N loss via denitrification is that large bottom areas of both of these systems are hypoxic for 5-6 months of the year. This suggestion is consistent with both the conceptual model of Kemp et al (2005) and with the finding that most denitrification is dependent of sediment nitrification for a nitrate source. Thus, if sediments of the Bay were to become more normoxic we would predict lower sediment recycling rates for both N and P.

Although denitrification is an anaerobic process, estuarine rates are often limited by conditions of low bottom water oxygen and organic enrichment of sediments. Resulting low redox conditions, high sulfide concentrations and shallow penetration of oxygen into sediments inhibit nitrification, and consequently denitrification (e.g., Vanderborght and Billen 1975; Henriksen and Kemp 1988; Joye and Hollibaugh 1995). Under these conditions, sediment recycling of N becomes more efficient in that most of the PN deposited to sediments is returned to the water column as NH_4 (Kemp et al 1990). We identified a very limited number of studies in which bottom water dissolved oxygen

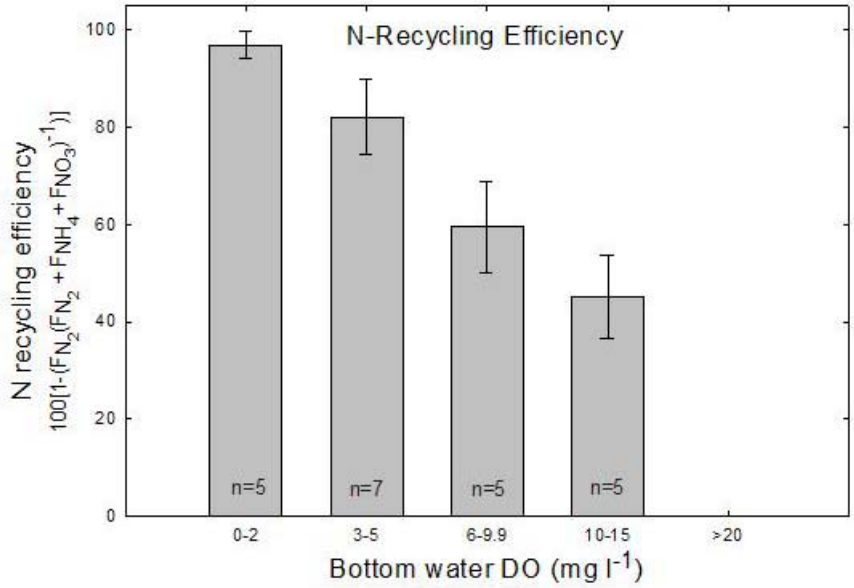

Figure 11-6. *Bar graph of N-recycling efficiency as a function of bottom water dissolved oxygen concentration. Bars were based on Chesapeake Bay data reported in Kemp et al (1990) and Cornwell (unpub. data). Terms in the recycling efficiency calculation (y-axis) are: F_{N2} = flux of N_2 from sediments; F_{NH4} = flux of ammonium from sediments; F_{NO3} = flux of nitrate from sediments.*

varied appreciably during the study period and in which denitrification and net sediment-water fluxes of NH_4, NO_2 and NO_3 were also measured. Such data were available from several studies conducted in Chesapeake Bay (Kemp et al 1990 and Cornwell, unpublished data). Based on these data we developed an index of N recycling efficiency and examined this as a function of bottom water dissolved oxygen concentrations (Fig. 11-6). There was a consistent increase in cycling efficiency as dissolved oxygen concentrations decreased. This trend suggests that estuarine eutrophication can seriously inhibit N-removal via coupled nitrification-denitrification. Clearly, more sites need to be examined to see if this is a general pattern of response. However, the increase in N cycling efficiency with low dissolved oxygen conditions is consistent with the relatively low percent N removal via denitrification in Chesapeake Bay and adjacent tributary rivers, all of which have hypoxic or anoxic bottom waters for portions of each year (Boynton et al 1995; Hagy et al 2004). We would predict that a larger portion of N contained in surficial sediments would be denitrified if deep water oxygen conditions improve due to management actions. The increase in denitrification activity is captured in the restoration trajectory

11-5. "Take Home" Summary

- Bottom water DO conditions have a clear impact on sediment N biogeochemistry.
- Indirect methods of analysis indicate that when sediments are exposed to normoxic conditions nitrogen is lost from the system, presumably via coupled nitrification-denitrification.
- Very limited but direct measurements of both routine sediment N fluxes and denitrification support this concept wherein N is lost in normoxic sediments.
- If bottom water DO conditions improve we would expect a significant decrease in sediment N recycling efficiency.

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Chapter 12

Statistical Analyses: Correlations and Multivariate Procedures

12-1. Background and Goals

Factors such as temperature, deep water 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 shown 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 correlation analyses on fluxes and associated environmental variables that potentially influence exchanges. We used the Pearson Correlation analysis package from SPSS 14.0 to examine the sediment flux data set. This is a simple survey technique and we did not expect to find especially strong correlations given the diversity of factors influencing sediment processes. However, we did expect to find hints as to which of many variables appeared to be involved in sediment flux regulation. We also employed a non-parametric technique for additional data analysis. As an exploratory step we used a technique called Classification and Regression Tree (CART®) analysis which is a non-parametric multivariate approach for prediction of both categorical (classification) and continuous (regression) variables. Within these analyses both categorical and continuous predictors can be used. We used the TREES module in the Systat® 10.2 software package with the least squares estimate for the loss function.

We view the analyses presented here as the beginning of a longer process of statistical analysis of the Chesapeake Bay sediment flux data set. In previous chapters we have presented many analyses of flux characteristics and patterns and the analyses presented here add to that effort.

12-2. Correlation Analyses

In this analysis we focused on correlations between the four major sediment fluxes (SOC, NH_4, NO_2 + NO_3 and PO_4) and environmental variables collected in the water column and sediments at the time sediment flux measurements were conducted. These environmental variables included the following: water depth, Secchi depth, bottom water temperature, salinity and DO concentration, bottom water concentrations of NO_2 + NO_3, PO_4, and NH_4, sediment Eh at 1 cm beneath the sediment surface, surficial sediment concentrations of PC, PN and PP and surficial sediment concentrations of active and total chlorophyll-a.

The results of these analyses are provided in Tables 12-1 through 12-5. We conducted five sets of correlation analyses. The first included all data in the sediment flux data set. The following four were sorted by salinity zone and included tidal freshwater sites (salinity <1.0), oligohaline sites (salinity 1.1 to 5), low mesohaline sites (salinity 5.1-15) and high mesohaline sites (salinity >15.1).

The general result of these analyses included the following: 1) correlation coefficients were rarely greater than 0.5 indicating that a great deal of the variability in

Table 12-1. *Results of correlation analyses for four major sediment fluxes and environmental site variables. This table includes the full sediment flux database.*

Full Data Correlations

		DO Flux:	DIP Flux:	NH4 Flux:	NO2+NO3 Flux:	Water Column Respiration
Station Depth:	Pearson Correlation	.477**	.118**	.020	.009	-.301**
	Sig. (2-tailed)	.000	.000	.433	.716	.000
	N	1506	1477	1492	1488	185
Secchi Depth:	Pearson Correlation	.372**	-.008	-.147**	.106**	-.389**
	Sig. (2-tailed)	.000	.766	.000	.000	.000
	N	1392	1379	1373	1382	186
Bottom Water Temperature:	Pearson Correlation	-.294**	.199**	.317**	.043	.040
	Sig. (2-tailed)	.000	.000	.000	.095	.586
	N	1498	1465	1478	1483	186
Salinity:	Pearson Correlation	.329**	.035	-.213**	.321**	.121
	Sig. (2-tailed)	.000	.184	.000	.000	.100
	N	1487	1454	1467	1472	186
Bottom Water DO:	Pearson Correlation	-.391**	-.347**	-.264**	.026	.117
	Sig. (2-tailed)	.000	.000	.000	.320	.112
	N	1464	1445	1445	1452	186
Bottom Water NO2+NO3:	Pearson Correlation	-.109**	-.151**	.008	-.516**	-.303**
	Sig. (2-tailed)	.000	.000	.756	.000	.000
	N	1466	1454	1450	1462	184
Bottom Water DIP:	Pearson Correlation	.150**	.378**	.194**	-.057*	.186*
	Sig. (2-tailed)	.000	.000	.000	.031	.012
	N	1471	1460	1455	1461	184
Bottom Water NH4:	Pearson Correlation	.333**	.274**	.317**	-.229**	-.194**
	Sig. (2-tailed)	.000	.000	.000	.000	.008
	N	1462	1450	1446	1453	184
Sediment Eh at 1 cm:	Pearson Correlation	-.348**	-.165**	-.125**	.031	-.200**
	Sig. (2-tailed)	.000	.000	.000	.259	.006
	N	1342	1338	1323	1344	186
Surficial Sediment PC%:	Pearson Correlation	-.043	.127**	.252**	-.222**	.189*
	Sig. (2-tailed)	.107	.000	.000	.000	.011
	N	1411	1382	1392	1402	182
Surficial Sediment PN%:	Pearson Correlation	.118**	.251**	.215**	-.124**	.117
	Sig. (2-tailed)	.000	.000	.000	.000	.116
	N	1354	1338	1333	1346	182
Surficial Sediment PP%:	Pearson Correlation	-.114**	.180**	.201**	-.250**	-.018
	Sig. (2-tailed)	.000	.000	.000	.000	.809
	N	1336	1327	1315	1334	182
Surficial Sed. Total Chlorophyll-a:	Pearson Correlation	.169**	.103**	.073**	-.035	.081
	Sig. (2-tailed)	.000	.000	.007	.192	.273
	N	1377	1370	1358	1376	184
Surficial Sed. Active Chlorophyll-a:	Pearson Correlation	.214**	.083**	.037	-.064*	.177*
	Sig. (2-tailed)	.000	.002	.174	.018	.017
	N	1349	1342	1330	1349	184

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 12-2. *Results of correlation analyses for four major sediment fluxes and environmental site variables. This table includes only stations with bottom water salinity less than or equal to 1 (tidal fresh).*

Tidal Fresh (<= 1) Correlations

		DO Flux:	DIP Flux:	NH4 Flux:	NO2+NO3 Flux:	Water Column Respiration
Station Depth:	Pearson Correlation	.210**	-.084	-.053	-.130	-.272
	Sig. (2-tailed)	.003	.256	.476	.074	.086
	N	191	183	183	191	41
Secchi Depth:	Pearson Correlation	.086	.019	-.099	.068	-.352*
	Sig. (2-tailed)	.246	.801	.191	.363	.024
	N	183	179	175	183	41
Bottom Water Temperature:	Pearson Correlation	-.418**	.232**	.290**	-.048	.132
	Sig. (2-tailed)	.000	.002	.000	.505	.412
	N	191	183	183	191	41
Salinity:	Pearson Correlation	.041	.136	-.111	.202**	.048
	Sig. (2-tailed)	.574	.066	.136	.005	.764
	N	191	183	183	191	41
Bottom Water DO:	Pearson Correlation	-.095	.161*	-.194**	.083	-.198
	Sig. (2-tailed)	.195	.029	.009	.261	.215
	N	187	183	179	187	41
Bottom Water NO2+NO3:	Pearson Correlation	.099	.096	-.005	-.460**	-.542**
	Sig. (2-tailed)	.177	.197	.942	.000	.000
	N	187	183	179	187	41
Bottom Water DIP:	Pearson Correlation	.051	.481**	-.022	-.224**	-.464**
	Sig. (2-tailed)	.491	.000	.773	.002	.002
	N	187	183	179	187	41
Bottom Water NH4:	Pearson Correlation	.038	.042	.379**	-.454**	.038
	Sig. (2-tailed)	.609	.575	.000	.000	.812
	N	187	183	179	187	41
Sediment Eh at 1cm:	Pearson Correlation	.017	-.142	-.124	.125	-.095
	Sig. (2-tailed)	.834	.084	.143	.128	.556
	N	150	149	142	151	41
Surficial Sediment PC%:	Pearson Correlation	-.085	-.081	.098	-.105	-.025
	Sig. (2-tailed)	.247	.283	.195	.152	.881
	N	186	178	178	186	39
Surficial Sediment PN%:	Pearson Correlation	-.010	.026	.094	-.150*	-.177
	Sig. (2-tailed)	.895	.733	.215	.043	.281
	N	182	178	174	182	39
Surficial Sediment PP%:	Pearson Correlation	-.017	.225**	.066	-.281**	-.269
	Sig. (2-tailed)	.818	.003	.390	.000	.097
	N	182	178	174	182	39
Surficial Sed. Total Chlorophyll-a:	Pearson Correlation	-.138	.248**	.087	-.045	.101
	Sig. (2-tailed)	.067	.001	.259	.556	.528
	N	177	173	169	177	41
Surficial Sed. Active Chlorophyll-a:	Pearson Correlation	-.095	.174*	.065	-.038	.345*
	Sig. (2-tailed)	.212	.022	.399	.612	.027
	N	176	172	168	176	41

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 12-3*. Results of correlation analyses for four major sediment fluxes and environmental site variables. This table includes only stations with bottom water salinity between 1 and 5 (oligohaline).*

Oligohaline (1 to 5) Correlations

		DO Flux:	DIP Flux:	NH4 Flux:	NO2+NO3 Flux:	Water Column Respiration
Station Depth:	Pearson Correlation	.278**	-.190*	-.146	.078	-.480*
	Sig. (2-tailed)	.000	.015	.062	.318	.020
	N	170	163	165	167	23
Secchi Depth:	Pearson Correlation	.022	-.106	-.051	.194*	-.659**
	Sig. (2-tailed)	.781	.188	.524	.015	.001
	N	161	155	156	158	23
Bottom Water Temperature:	Pearson Correlation	-.394**	.225**	.385**	.188*	.135
	Sig. (2-tailed)	.000	.004	.000	.015	.539
	N	170	163	165	167	23
Salinity:	Pearson Correlation	-.080	.053	.016	.141	.032
	Sig. (2-tailed)	.297	.500	.841	.070	.883
	N	170	163	165	167	23
Bottom Water DO:	Pearson Correlation	.044	.080	-.054	-.028	-.106
	Sig. (2-tailed)	.572	.308	.489	.722	.630
	N	170	163	165	167	23
Bottom Water NO2+NO3:	Pearson Correlation	.318**	-.221**	-.305**	-.293**	-.505*
	Sig. (2-tailed)	.000	.005	.000	.000	.014
	N	170	163	165	167	23
Bottom Water DIP:	Pearson Correlation	-.075	.595**	.139	-.191*	.242
	Sig. (2-tailed)	.330	.000	.077	.014	.267
	N	169	163	164	166	23
Bottom Water NH4:	Pearson Correlation	.105	.289**	.037	-.170*	-.362
	Sig. (2-tailed)	.175	.000	.634	.028	.089
	N	170	163	165	167	23
Sediment Eh at 1 cm:	Pearson Correlation	-.040	.087	-.139	.066	-.356
	Sig. (2-tailed)	.615	.287	.086	.411	.096
	N	159	153	154	158	23
Surficial Sediment PC%:	Pearson Correlation	.029	.073	.081	-.216**	.642**
	Sig. (2-tailed)	.712	.355	.301	.005	.001
	N	169	162	164	166	23
Surficial Sediment PN%:	Pearson Correlation	-.201**	.326**	.289**	-.217**	.399
	Sig. (2-tailed)	.009	.000	.000	.005	.060
	N	167	161	162	164	23
Surficial Sediment PP%:	Pearson Correlation	-.182*	.461**	.260**	-.212**	-.053
	Sig. (2-tailed)	.019	.000	.001	.007	.811
	N	165	159	160	162	23
Sediment Total Chlorophyll-a:	Pearson Correlation	.019	.154	.149	.022	-.078
	Sig. (2-tailed)	.810	.058	.066	.787	.724
	N	159	153	154	156	23
Sediment Active Chlorophyll-a:	Pearson Correlation	.101	.131	.097	-.004	.360
	Sig. (2-tailed)	.207	.108	.233	.957	.092
	N	157	151	152	154	23

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 12-4. *Results of correlation analyses for four major sediment fluxes and environmental site variables. This table includes only stations with bottom water salinity between 5 and 15 (low mesohaline).*

Low Mesohaline (5 - 15) Correlations

		DO Flux:	DIP Flux:	NH4 Flux:	NO2+NO3 Flux:	Water Column Respiration
Station Depth:	Pearson Correlation	.380**	.044	.084*	-.280**	-.412**
	Sig. (2-tailed)	.000	.249	.027	.000	.000
	N	683	679	688	682	85
Secchi Depth:	Pearson Correlation	.217**	-.105**	-.178**	-.122**	-.513**
	Sig. (2-tailed)	.000	.007	.000	.002	.000
	N	652	657	657	654	86
Bottom Water Temperature:	Pearson Correlation	-.152**	.237**	.315**	.247**	.147
	Sig. (2-tailed)	.000	.000	.000	.000	.176
	N	684	680	689	683	86
Salinity:	Pearson Correlation	.292**	-.070	-.101**	.100**	-.446**
	Sig. (2-tailed)	.000	.066	.008	.009	.000
	N	684	680	689	683	86
Bottom Water DO:	Pearson Correlation	-.419**	-.331**	-.343**	.282**	.296**
	Sig. (2-tailed)	.000	.000	.000	.000	.006
	N	672	677	677	673	86
Bottom Water NO2+NO3:	Pearson Correlation	.047	-.189**	-.200**	-.455**	-.153
	Sig. (2-tailed)	.227	.000	.000	.000	.166
	N	672	677	677	674	84
Bottom Water DIP:	Pearson Correlation	.193**	.350**	.268**	.082*	.171
	Sig. (2-tailed)	.000	.000	.000	.034	.121
	N	673	678	678	674	84
Bottom Water NH4:	Pearson Correlation	.460**	.237**	.336**	-.265**	-.266*
	Sig. (2-tailed)	.000	.000	.000	.000	.015
	N	664	669	669	666	84
Sediment Eh at 1 cm:	Pearson Correlation	-.412**	-.190**	-.179**	.102**	-.103
	Sig. (2-tailed)	.000	.000	.000	.009	.347
	N	647	653	652	650	86
Surficial Sediment PC%:	Pearson Correlation	.110**	.183**	.313**	-.233**	.018
	Sig. (2-tailed)	.005	.000	.000	.000	.873
	N	635	629	638	633	84
Surficial Sediment PN%:	Pearson Correlation	.237**	.224**	.186**	-.213**	-.064
	Sig. (2-tailed)	.000	.000	.000	.000	.565
	N	613	616	616	614	84
Surficial Sediment PP%:	Pearson Correlation	.041	.186**	.181**	-.152**	.082
	Sig. (2-tailed)	.310	.000	.000	.000	.461
	N	606	610	609	608	84
Sediment Total Chlorophyll-a:	Pearson Correlation	.228**	.048	.069	-.166**	-.011
	Sig. (2-tailed)	.000	.219	.077	.000	.922
	N	644	650	649	647	84
Sediment Active Chlorophyll-a:	Pearson Correlation	.305**	.052	.051	-.187**	.154
	Sig. (2-tailed)	.000	.193	.203	.000	.163
	N	629	635	634	633	84

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 12-5*. Results of correlation analyses for four major sediment fluxes and environmental site variables. This table includes only stations with bottom water salinity greater than 15 (high mesohaline).*

High Mesohaline (> 15) Correlations

		DO Flux:	DIP Flux:	NH4 Flux:	NO2+NO3 Flux:	Water Column Respiration
Station Depth:	Pearson Correlation	.590**	.263**	.295**	-.197**	-.566**
	Sig. (2-tailed)	.000	.000	.000	.000	.000
	N	442	428	430	431	36
Secchi Depth:	Pearson Correlation	.447**	.036	.047	-.155**	-.574**
	Sig. (2-tailed)	.000	.484	.363	.002	.000
	N	394	386	383	385	36
Bottom Water Temperature:	Pearson Correlation	-.324**	.201**	.306**	-.021	.618**
	Sig. (2-tailed)	.000	.000	.000	.662	.000
	N	442	428	430	431	36
Salinity:	Pearson Correlation	-.190**	-.114*	-.216**	.038	-.095
	Sig. (2-tailed)	.000	.019	.000	.431	.582
	N	442	428	430	431	36
Bottom Water DO:	Pearson Correlation	-.484**	-.551**	-.556**	.335**	.667**
	Sig. (2-tailed)	.000	.000	.000	.000	.000
	N	433	420	422	423	36
Bottom Water NO2+NO3:	Pearson Correlation	.191**	-.157**	-.128**	-.441**	-.326
	Sig. (2-tailed)	.000	.001	.008	.000	.053
	N	433	424	422	427	36
Bottom Water DIP:	Pearson Correlation	.414**	.547**	.391**	-.011	-.369*
	Sig. (2-tailed)	.000	.000	.000	.819	.027
	N	437	428	426	427	36
Bottom Water NH4:	Pearson Correlation	.513**	.477**	.355**	-.014	-.196
	Sig. (2-tailed)	.000	.000	.000	.780	.253
	N	436	427	425	426	36
Sediment Eh at 1 cm:	Pearson Correlation	-.276**	-.242**	-.248**	.122*	-.357*
	Sig. (2-tailed)	.000	.000	.000	.017	.033
	N	383	380	372	382	36
Surficial Sediment PC%:	Pearson Correlation	-.032	.238**	.327**	-.188**	.746**
	Sig. (2-tailed)	.514	.000	.000	.000	.000
	N	417	407	405	410	36
Surficial Sediment PN%:	Pearson Correlation	.082	.316**	.445**	-.275**	.599**
	Sig. (2-tailed)	.104	.000	.000	.000	.000
	N	389	380	378	383	36
Surficial Sediment PP%:	Pearson Correlation	.056	.168**	.201**	-.074	.529**
	Sig. (2-tailed)	.276	.001	.000	.152	.001
	N	380	377	369	379	36
Sediment Total Chlorophyll-a:	Pearson Correlation	.285**	.113*	.089	-.003	.095
	Sig. (2-tailed)	.000	.028	.087	.954	.582
	N	384	381	373	383	36
Sediment Active Chlorophyll-a:	Pearson Correlation	.252**	.110*	-.006	.002	.162
	Sig. (2-tailed)	.000	.034	.915	.970	.345
	N	374	371	363	373	36

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

the flux variable was not explained by any one environmental variable; 2) because there were so many observations of flux and associated environmental variables (~1500 for each in the full data set) there were many correlations that were statistically significant; 3) the significant correlations, while not very predictive, were almost always consistent with the conceptual models referred to in earlier portions of this report regarding mechanisms controlling sediment fluxes; 4) there was more consistency in significant correlations among salinity zones than sharp differences indicating the general importance of a limited number of variables and 5) deep water dissolved nutrient concentrations were almost always significantly correlated with the associated flux (i.e., ammonium flux was positively correlated with bottom water ammonium concentrations).

As expected, bottom water temperature and DO concentrations were significantly correlated with most sediment fluxes in all salinity zones. The temperature relationships were expected because of the influence of temperature on molecular diffusion and metabolic rates. Some fluxes (NH_4 and PO_4) were enhanced while others were reduced (SOC, NO_2 + NO_3) due to the influence of low DO conditions. For example, there is a strong relationship between redox conditions and the formation of FeOOH-PO_4 complexes. Under oxic conditions P will adsorb to Fe^{3+} but will desorb under anoxic conditions (Krom and Berner 1980; Sundby et al 1992). In this analysis substantial PO_4 fluxes were a warm season event and were substantial in those regions of the bay experiencing hypoxic or anoxic conditions. To further emphasize the environmental conditions conducive to sediment P release, P releases were inversely correlated with sediment Eh, again consistent with hypoxic/anaoxic conditions and large sediment P releases. SOC rates were also influenced by DO conditions with rates being smaller at lower DO concentrations. SOC was also positively correlated with temperature, likely for the reason provided above and inversely correlated with depth because of the strong association of depth with bottom water DO concentrations. A similar, but more complex, situation may exist for sediment nitrogen dynamics. Ammonium production appears to respond to temperature increases and to increasing organic matter supply, although we did not measure organic matter supply rate at most monitoring sites. Some of this NH_4 may be converted to NO_3 via nitrification in the presence of sufficient DO (Nedwell et al 1983; Kemp et al 1990); however, in low DO situations nitrification is suppressed or totally blocked (Henriksen and Kemp 1988) in which case all of the ammonium produced can be released from sediments. Inhibition of nitrification may have served to enhance ammonium fluxes in the seasonally hypoxic or anoxic regions (Kemp et al 1990). Sediment ammonium and phosphate fluxes in most salinity zones were correlated with bottom water concentrations of these compounds. These correlations likely resulted from sediment nutrient release rates adding to the nutrient stock in the water column rather than the water column nutrient concentrations having any strong bearing on the magnitude of these fluxes. However, concentrations of DO have a strong negative effect on SOC rates (DO becomes rate limiting) and nitrite plus nitrate fluxes certainly respond to concentrations of these compounds in the water column. When water column nitrite plus nitrate concentrations are elevated (i.e., from spring river runoff) these compounds move from the water column to sediments and the nitrate entering sediments is likely denitrified in anoxic sediment zones.

It is encouraging that correlation analyses suggested several variables as being generally important in influencing sediment nutrient and oxygen exchanges. Furthermore, these same environmental variables appear to play a role in most salinity zones. However, these results are not strong predictors of sediment processes. In particular, sediment properties (e.g., PC, PN, PP and chlorophyll-a) were not generally significant predictors of sediment flux. This result was initially thought to be in conflict with conceptual models of sediment processes. Other researchers (Cowan and Boynton 1996; Kemp et al 1997; Stankelis et al 1998) found strong evidence that organic matter supply exerts a strong effect on sediment processes. However, in these cases, sediment properties related to organic matter were measured prior to measurement of sediment fluxes. For example, Cowan and Boynton (1996) and Stankelis et al (1998) used measurements of sediment chlorophyll-a sampled immediately after deposition of the spring diatom bloom (mid May) as a predictor of summer (June – August) sediment flux of dissolved nutrients. Boynton and Kemp (2000) used a similar approach and found similar results. In short, a lag was invoked between peak times of organic matter supply rates (spring bloom deposition) and sediment flux (mainly in summer when temperature was high enough to support intense microbial activity). In the Chesapeake Bay data set virtually all environmental variables were measured at the same time as sediment fluxes and, for the most part (~72%), were made during summer periods. Thus, we are interpreting most flux measurements without the benefit of knowing how much labile organic matter reached the sediments during the peak spring deposition period, prior to flux measurement. However, in cases where those spring measurements were made, the case for sediment properties being important factors influencing sediment flux is clearly established.

12-3. Classification and Regression Analyses (CART®)

This non-parametric, multivariate approach was applied to several aspects of the Chesapeake Bay sediment flux data set. First, each flux (SOC, NH_4, PO_4, and NO_2 + NO_3) was used as the variable to be predicted and all other data (except other fluxes and the categorical variable "tributary") were used as input variables. The full data set was utilized. The data set was then sorted into salinity regimes and the same procedure repeated (the variable "tributary excluded and bottom water N and P concentrations were excluded in predictions of ammonium and phosphate flux). Data were sorted into tidal freshwater, oligohaline, low mesohaline and high mesohaline groups with the same salinity criteria used earlier.

We should note that there is really no end to the possible arrangements of data and variables that could be used in variations of CART® analyses. In this effort we tended to be inclusive, rather than restrictive, regarding variable selection, even to the point of allowing variables to enter the regression tree when there was no obvious and direct connection to mechanisms influencing sediment fluxes. Some indirect relationship might exist. Future work might entail a different approach to variable selection.

Regression trees using the full data set were generally weaker than those for specific salinity zones, often by a large margin (Table 12-6). However, most variables entering the analysis were expected. For example, SOC rates split into large and small groups based on depth (SOC larger at depths < 9 m) and with bottom water DO concentrations greater than 2.9 mg l^{-1}. Similarly, phosphate fluxes were larger when

bottom water DO was less than 2.9 mg l^{-1}. Nitrite plus nitrate fluxes were more positive when bottom water nitrite plus nitrate concentrations were less than 8.3 µM.

Table 12-6*. Proportional reduction in error coefficients derived from classification and regression analysis of sediment water fluxes. These coefficients are roughly equivalent to* R^2 *values used in traditional linear regression analyses.*

	SOC	PO_4	NH_4	$NO_2 + NO_3$
Full Data Set	0.36	0.28	0.20	0.28
Tidal Freshwater (< 1)	0.52	0.46	0.38	0.48
Oligohaline (1 – 5)	0.29	0.55	0.52	0.27
Low Mesohaline (5 – 15)	0.43	0.15	0.33	0.45
High Mesohaline (> 15)	0.76	0.35	0.43	0.46

In tidal freshwaters similar variables entered the regression tree but the amount of variability explained increased (Fig. 12-1). Temperature and sediment properties entered for SOC. Importantly, SOC rates were not DO concentration limited when bottom water DO was above 2.9 mg l^{-1}. Sediment ammonium flux was influenced by temperature (higher fluxes at temperature > 28 C) and low bottom water dissolved oxygen conditions (DO< 3.3 mg l^{-1}). Nitrite plus nitrate fluxes were elevated when bottom water N concentrations were high.

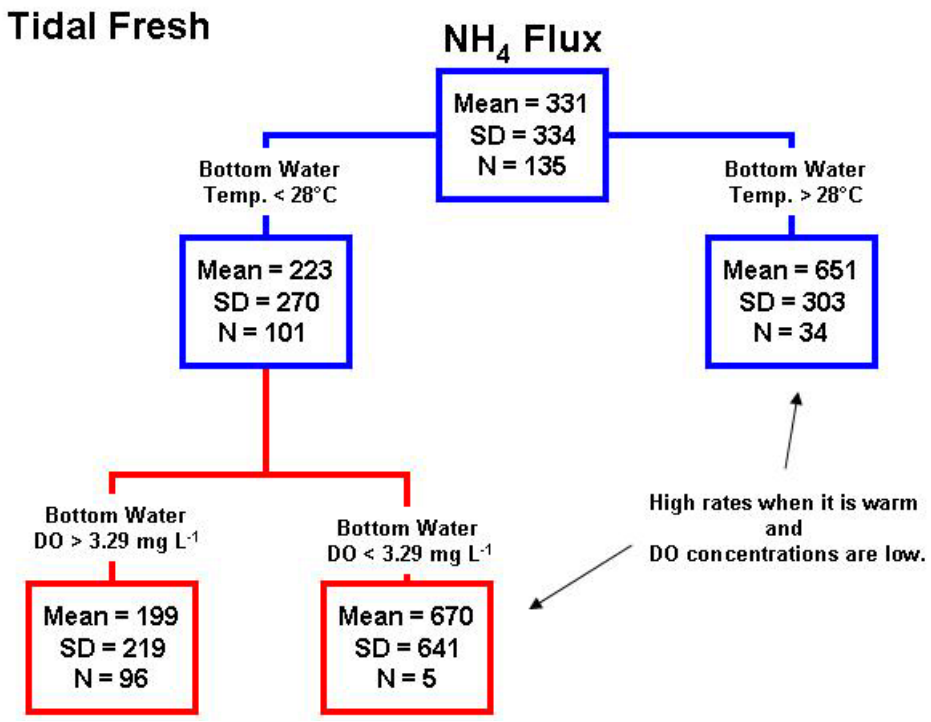

Figure 12-1. *Graphic results of classification and regression analysis for sediment* NH_4 *flux at tidal freshwater sites contained in the Chesapeake Bay sediment flux dataset. Variable selection explained in the text.*

In oligohaline waters SOC rates were elevated at depths < 10 m and at elevated water temperature (> 26 C). Phosphate fluxes were greater at sites with higher sediment PP concentrations and depressed bottom water DO concentrations. Ammonium fluxes were higher at higher temperature and at sites with elevated sediment organics. Again, nitrite plus nitrate fluxes were larger (more negative: directed into sediments) at shallow depths and at high water column nitrite plus nitrate concentrations.

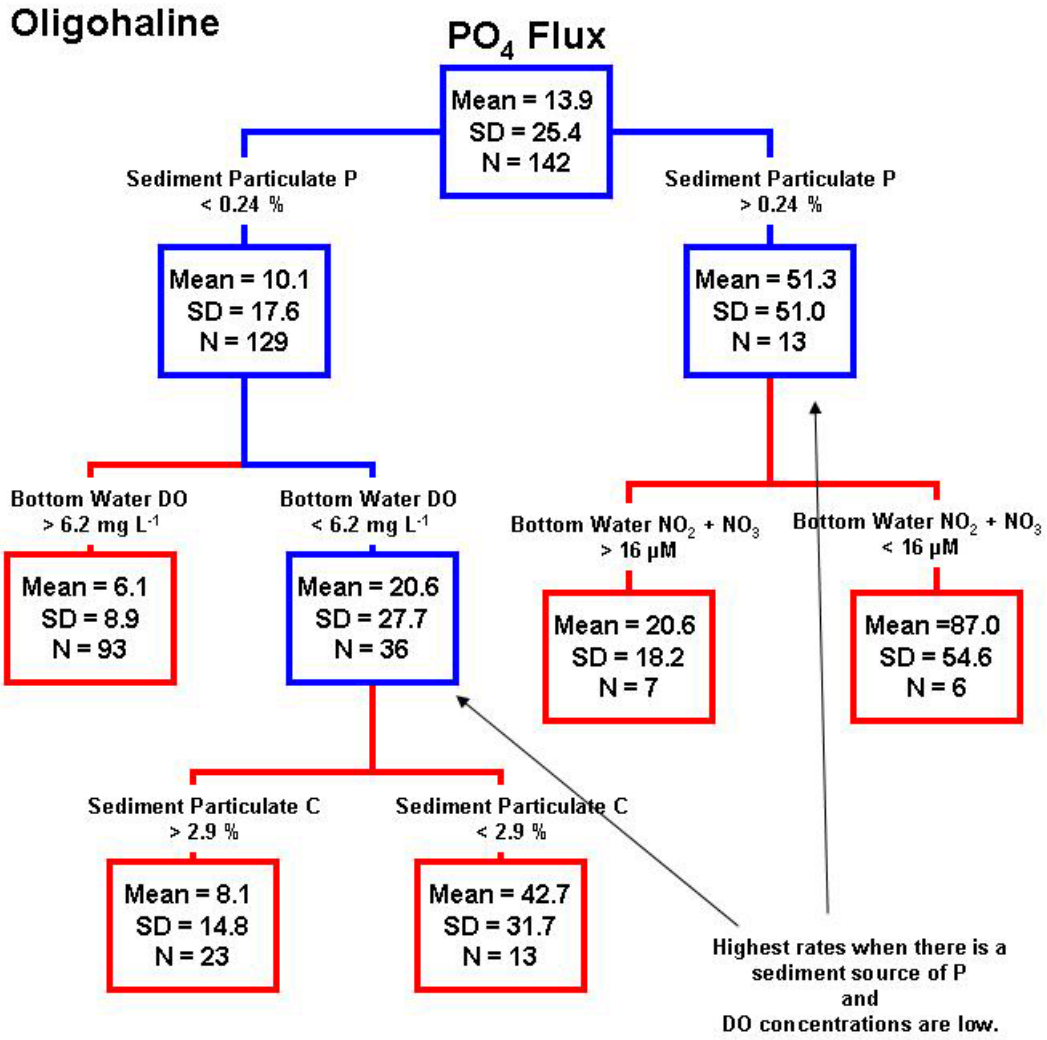

Figure 12-2. *Graphic results of classification and regression analysis for sediment PO_4 flux at oligohaline sites contained in the Chesapeake Bay sediment flux dataset. Variable selection explained in the text.*

At the low and high mesohaline sites SOC rates were lower when bottom water DO concentrations were low (< 3.1 mg l^{-1}) and were higher at sites having more positive Eh values (>359 mV) and high bottom water DO concentrations. Sediment P flux was elevated when DO concentrations were low (< 2.5 mg l^{-1}) and at higher temperature and sediment PP content. Ammonium flux was high when sediment PC content was very high (> 7.5 %) and when bottom water DO concentrations were low (< 5.3 mg l^{-1}). Finally, nitrite plus nitrate flux were less negative (more tendency for N to move from

sediments to the water) when bottom water nitrite plus nitrate concentrations were less than 12 µM and bottom water DO concentrations > 3.7 mg l^{-1}.

Several regression tree diagrams are shown in Figures 12-1 through 12-4. Summary statistics for these analyses are provided in Table 12-6 and these values represent something close to R^2 values from traditional regression analyses.

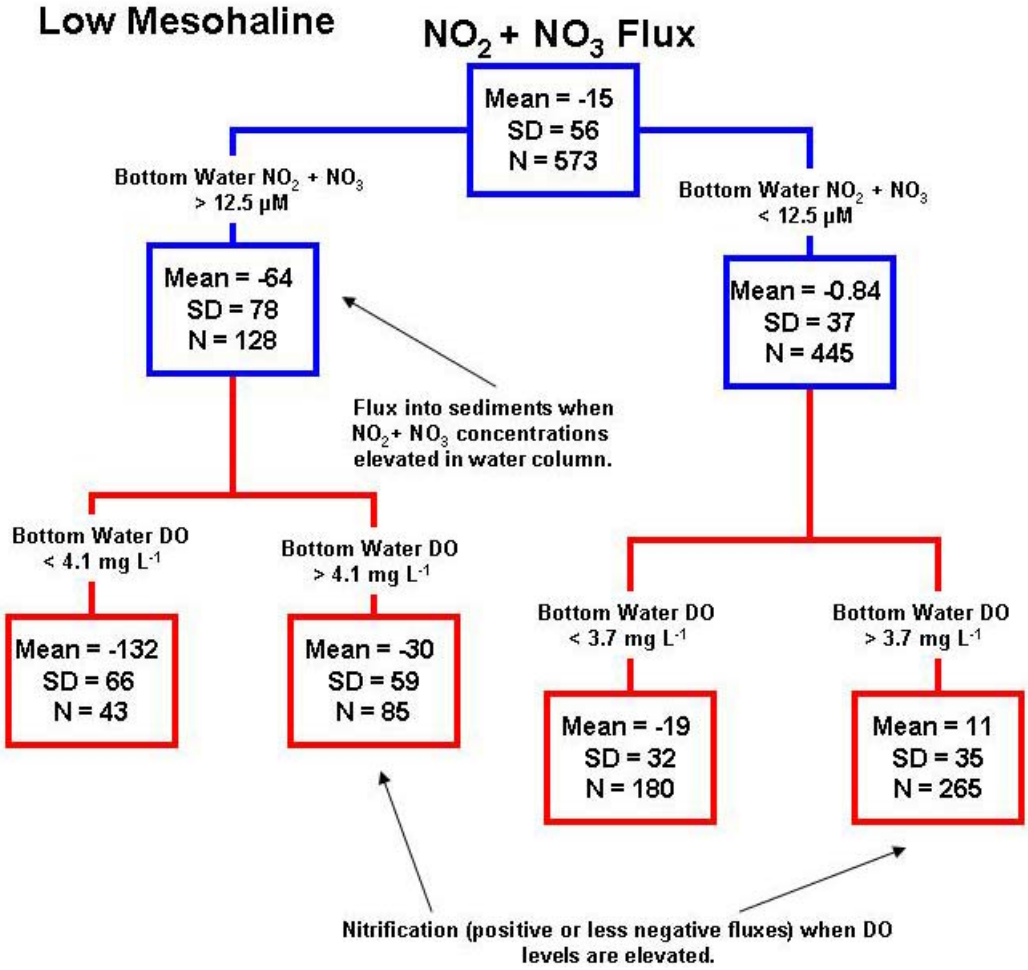

Figure 12-3. *Graphic results of classification and regression analysis for sediment NO_2 + NO_3 flux at low mesohaline sites contained in the Chesapeake Bay sediment flux dataset. Variable selection explained in the text.*

Consideration of multiple variables improved the amount of variance in fluxes that could be explained and the additional variables were consistent with conceptual models of estuarine sediment flux. Our view is that if we had the benefit of more seasonal data (fluxes measured in spring and fall) and sediment properties measured prior to the period of high sediment fluxes the portion of variance that could be explained could be increased even further.

One of the central findings to emerge from these analyses is that there appear to be a few "master variables" influencing sediment flux as opposed to many variables. Furthermore, these influencing variables seem to be important in most salinity zones of the Bay and tributary rivers. For example, temperature is clearly of general importance for most fluxes. Dissolved oxygen concentration (and sediment Eh conditions) in bottom

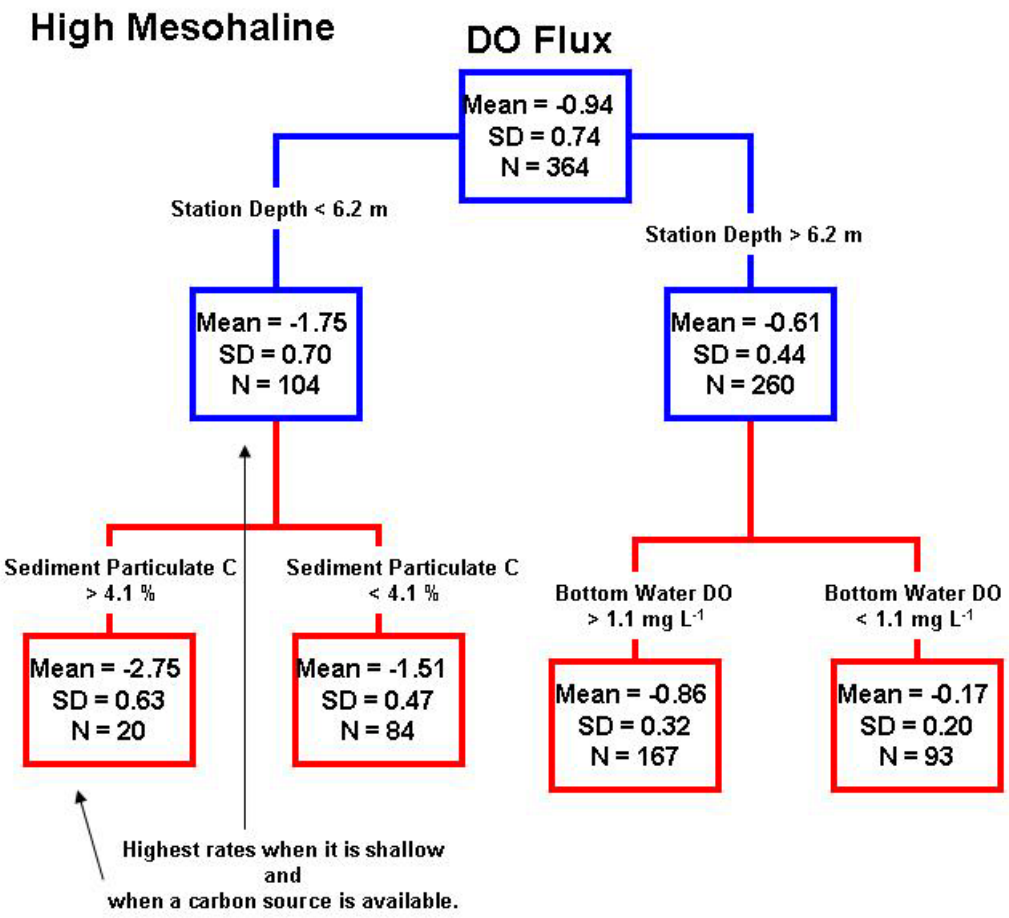

Figure 12-4. *Graphic results of classification and regression analysis for sediment SOC (labeled as DO Flux in this figure to remain consistent with database variable labels) at high mesohaline sites contained in the Chesapeake Bay sediment flux dataset. Variable selection explained in the text.*

waters and sediments is also clearly important. Nitrite plus nitrate concentration has an important influence of the magnitude and direction of nitrite plus nitrate flux. Second, dissolved oxygen concentration in deep water was often a splitting variable and the concentration of DO at the splitting point is of interest. In many cases the critical DO concentration is about 3-4 mg l^{-1}. At lower DO concentrations nitrite plus nitrate flux is almost never positive (positive flux is indicative of the all important coupling of nitrification to denitrification), sediment ammonium flux changes from modest to very large and sediment P flux does the same thing. Thus, from a management viewpoint, increasing bottom water DO concentrations during summer to something between 3 and 4 mg l^{-1} is likely to have a massive impact on sediment processes. We suggest that DO elevation, to even these modest levels (which are less than the 5 mg l^{-1} criteria for many Bay habitats), would have the effect of starting Bay sediments on a restoration trajectory (Fig. 1-1) as opposed to being stuck in the degradation trajectory which is the current condition.

12-4. "Take Home" Summary

- Several statistical analyses suggest a few important water quality variables have strong influence of sediment flux
- These variables (e.g., bottom water DO, temperature, sediment Eh, water column nitrite plus nitrate concentrations) appear to be important in all salinity zones of the Bay and tributary rivers
- It is very likely that organic matter deposition rates, particularly during spring, set the upper limit on sediment flux and further modify the nature of sediment flux. We do not have estimates of spring deposition at most sites in this data set so this important process is not directly included in these analyses. However, regression modeling (see Chapter 6) has indicated this to be the case
- The conceptual model of sediment flux is consistent with results of these statistical analyses. It also appears that modest improvement in deep water DO conditions (> 3-4 mg l^{-1} during summer) would strongly modify sediment flux such that nutrient recycling rates would decrease and thus contribute to improved water quality conditions.

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