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Editors

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Introduction

Perpectives on Chesapeake Bay, 1994 **is the fourth in a series of literature syntheses being published by the Chesapeake Bay Program's Scientific and Technical Advisory Committee (STAC). The purpose of the series is to p rovide managers, scientists, legislators, and others with informative summaries on research findings and other issues that bear on the Chesapeake Bay Program's efforts to restore the nation's largest estuary.**

This volume consists of four papers. Ranging literally over land, sea, and air, they not only reflect the diversity of scientific inquiry that is shaping the restoration effort but they also reveal the pervasiveness of two common themes. One is that the anthropogenic factor looms large in any scientific inquiry into the workings of the Chesapeake Bay ecosystem, with each paper providing a scientific perspective on the direct and indirect effects of human activity on estuarine structure and function.

The tables in this report are under construction. Thank you.

The Role of Nitrogen and Phosphorus in Chesapeake Bay Anoxia

Thomas R. Fisher and Arthur J. Butt

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1. Introduction

Anoxia in aquatic systems is intimately linked to primary production and nutrient limitation. Although primary production results in oxygen production in surface waters, oxygen concentrations are raised above the saturation level, and the excess gas escapes to the atmosphere (e.g., Kemp et al. 1992). When organic matter sinks into bottom waters, which have only a limited oxygen supply, metabolic consumption of the organic matter consumes the oxygen. Anoxia is the result of the metabolic consumption of oxygen in aphotic bottom waters of lakes, estuaries, and oceans in excess of the oxygen provided by physical circulation. Anoxia usually occurs during the warmer months, when the supply of oxygen is reduced by low solubility and thermal stratification. Under these conditions, the consumption of oxygen is also high owing to elevated metabolic rates. The severity and duration of anoxia are determined in part by the rate of production of organic matter, which is in turn controlled by the availability of light or a limiting nutrient (e.g., Harding et al. 1992). This sequence of events is summarized in figure 1.

The supply of light and nutrients regulates the production of phytoplankton-derived organic matter. The nutrient supply is usually the most important process determining net primary production in aquatic systems (Howarth 1988), whereas light is an important regulator of algal production only in turbid environments, usually with excess nutrients and low biomass accumulation (Wofsy 1983, Cloern 1987). Nutrient limitation, therefore, controls the production of organic matter that fuels bottomwater anoxia.

Chesapeake Bay is a large estuary that annually experiences summer anoxia (Taft et al. 1980, U.S. Environmental Protection Agency 1982, Seliger et al. 1985, Malone et al. 1988, Cooper and Brush 1991, Malone 1992, Harding et al. 1992). There are local, regional, and national efforts under way to reduce the duration and severity of anoxia in the Bay (e.g., Magnien et al. 1987), and reduction of nutrient inputs is the central strategy being employed in the joint anoxia- reduction efforts of the three states (Maryland, Pennsylvania, and Virginia) that account for most of the Chesapeake watershed.

The organic matter that creates anoxia in the bottom waters of Chesapeake Bay is supplied by two primary internal sources. As in lakes and oceanic basins, there is a vertical supply of organic matter derived from sedimentation

from local surface waters. However, as an enclosed estuary, the Bay has a countercurrent circulation (Pritchard 1952) that provides particulate and dissolved organic matter from the estuary as a whole by means of a landward subpycnocline transport (see stippled arrows in figure 2). The supply of organic matter that creates anoxia in bottom waters therefore may have two controls(1) nutrient limitation in local surface waters regulating the vertical sedimentation flux, and (2) nutrient limitation in the estuary as a whole (on a larger spatial scale) that controls the amount of organic matter that sediments from surface waters into bottom waters and is subsequently transported in the landward subpycnocline flow in a particulate or dissolved form. Accordingly, this paper examines the relative importance of nutrient limitation of algal growth and biomass accumulation on both the *local* scale and the *estuarine* scale.

2. Nutrient Limitation

Many processes control the growth and accumulation of algae in aquatic systems. Light is essential for photosynthesis, and plant nutrients such as inorganic forms of nitrogen (N), phosphorus (P), silicon (Si), trace metals, and vitamins are required to sustain growth rates. The availability of light and nutrients limits algal growth rates, and other processes (e.g. advective losses, grazing, sinking, and cell death) may control biomass accumulation by removing biomass after it is produced.

Nutrient limitation must be considered at different scales for algal growth rates and biomass accumulation. The rate of algal growth is the rate of production of new algal biomass prior to losses; the growth rate may be constrained by the supply of light or a limiting nutrient. The accumulation rate of algal biomass is the net rate at which algal biomass increases after losses are subtracted from production. The rate of biomass accumulation may be constrained by the supply of a nutrient on a scale larger than that which governs growth, depending on the relative magnitudes of growth, loss, and advection.

To begin, it is useful to first consider nutrient limitation of algal growth rates. If light and nutrients are available in excess (as in a culture or spring bloom), then intracellular stores of nutrients are filled to capacity, and uptake of extracellular nutrients provides the supply to intracellular pools. The growth rate of the algae is determined only by assimilation of abundant components in the assembly of new cellular material at the maximum growth rate, which

is primarily determined by temperature (figure 3)(Eppley 1972). However, if one of the externally required nutrients is available at less than the rate required for maximum cell growth, then the extracellular and intracellular pools decrease as biomass accumulates, and intracellular storage of the limiting element is mobilized. Algal growth continues at a reduced rate by (1) uptake of the limiting nutrient from a diminishing extracellular pool, (2) mobilization of intracellular stores, and (3) redeployment of existing intracellular pools (Wheeler 1983, Lean and Cuhel 1987).

Under nutrient-limited conditions, there may be little relationship between algal growth rates and extracellular nutrient concentrations. Owing to mobilization of intracellular pools, growth rates are often more closely related to the sum of intracellular nutrient pools and storage, also known as the cell quota (Q)(Eppley and Strickland 1968). When the intracellular storage is exhausted and intracellular nutrient pools are at minimum levels, growth rates are regulated by the external rate of supply of the limiting nutrient. When supply rates and growth rates are closely coupled under nutrient depletion, there may be little apparent relationship between extracellular nutrient concentrations (at trace levels) and algal growth rates owing to continuous uptake by nutrient- starved algae.

These relationships were largely derived from cultures of microalgae under varying conditions of nutrient supply. Droop (1983) has summarized the effects of extracellular nutrient concentration ([nutrient], micromole or microg l-1) and cell quota (pmole or pg cell-1) on algal growth rates (pnu, d-1) as follows

$$pnu = Pnu_{(sub\ max)} * [nutrient]/([nutrient] + K_{nutrient})$$

(eq. 1)

$$pnu = Pnu_{(sub\ max)} * (1-Kq/Q)$$

(eq. 2)

where pnu(max) is the maximum growth rate (d-1), Knutrient is the half-saturation constant (micromol or microg l-1) for uptake of the nutrient, and Kq is the minimum cell quota required for cell maintenance (intracellular nutrient pools + cellular storage, pmol or pg cell-1, see figure 3). Equations 1 and 2 are hyperbolas, with strong dependence of growth rates on [nutrient] and Q at values of [nutrient] and Q lower than Knutrient and Kq, respectively, but there is little or no relationship between growth rates and [nutrient] or Q when these are more than two times Knutrient and Kq.

The presence of intracellular storage introduces time lags into the onset of nutrient limitation of growth rate. As the extracellular pool becomes smaller, intracellular storage and pools are reduced; however, there may be a time delay between depletion of the extracellular pool of a limiting nutrient and a restricted rate of growth owing to mobilization of the intracellular stores, as described above. This delay is particularly true in the case of P, which is stored as condensed polyphosphate granules, the mobilization of which may make possible as many as 5(sup -10) cell divisions without external sources of P (Reynolds 1984). However, phytoplankton have a much smaller capacity to store N, Si, and other potentially limiting elements (Kana and Glibert 1987, Lean et al. 1989). The ratio Qmax/k(sub q) (where Qmax is the maximum cell quota) is a measure of the ability of algae to store a potentially limiting element. For the N and P content of microalgae, Qmax/k(sub q) is about 2 and 10, respectively (Droop 1974, Dortch et al. 1985); however, macroalgae appear to have a somewhat greater capacity to store N, with Qmax/k(sub q) for N of 3(sup -5) (Fujita et al. 1989). These values can be interpreted as both the storage capability for N and P as well as the physiological flexibility to function under conditions of extracellular N and P depletion.

More than one nutrient may be potentially limiting the rate of algal growth. If more than one nutrient is available at less-than-optimum rates, then the one in shortest supply is the most limiting one and determines the growth rate. This is Liebig's law of the minimum (Liebig 1840), a simple 19th-century rule for the effects of different factors on terrestrial plant yields that later was applied to the growth of phytoplankton by Blackman (1905). However, dual limitation by both N and P or P and Si is commonly reported in nutrient addition bioassays (e.g., Morris and Lewis 1988, Dodds and Priscu 1990, Fisher et al. 1992b). Dual limitation may occur more frequently than expected because bioassay tests of nutrient limitation often span several days, and growth rate limitation may switch from one nutrient to the other during the incubation period because of the relative proportions of nutrients that are added.

Light limitation is a special case of the resource limitation described above. Insufficient light for algal growth is encountered when incident irradiance is low, turbidity is high, and the surface mixed layer is deep, with the result that phytoplankton are exposed to insufficient energy for net growth. Most aquatic systems have at least some of these characteristics in winter, and the turbid, flowing waters of larger rivers, some reservoirs, and the low-salinity regions of estuaries usually have these characteristics continuously (Wofsy 1983, Harding et al. 1986, Grobbelaar 1990). Often accompanying these conditions are relatively high concentrations of nutrients. Under light limitation, internal nutrient pools are usually filled to capacity, yet growth rates are very low and limited by the availability of light. Wofsy (1983) and Grobbelaar (1990) have developed models that describe the production, growth, and biomass accumulation of phytoplankton under these conditions. In general, the greater the nonalgal turbidity in the surface mixed layer, the less algal biomass that develops when all light has been extinguished in the surface mixed layer. The Wofsy model provides a simple test of light limitation based on field measurements such as Secchi depth or extinction coefficient, algal biomass as *chlorophyll a*, and depth of the surface mixed layer obtained from vertical profiles of density.

Nutrient limitation of algal growth is more commonly encountered in less turbid waters.

Under nutrient limitation, algae are unable to consume all available light. Growth rates are then limited by the supply of the limiting nutrient in the presence of excess light. Under these conditions, as described above, extracellular nutrient concentrations may be at detection limits over a broad range of growth rates owing to rapid algal uptake under nutrient limited conditions.

The analogy of a batch culture has been used to describe nutrient limitation of algal growth. In natural populations, with varying physiological characteristics of uptake and intracellular storage, the additional concept of competition between populations must be included because of the selective pressure applied by extreme nutrient depletion. Species or populations that grow fastest under the ambient conditions tend to dominate; smaller algal species often have a competitive advantage because they tend to have lower values of Knutrient and Kq. Some algal species (e.g., diatoms) may be limited by Si, whereas others do not require this element and may flourish under Si depletion. These changes in community structure occur at larger temporal and spatial scales (i.e., days to weeks, and km), and result in seasonal changes which may be difficult to predict because of processes such as selective grazing.

The accumulation of algal biomass requires consideration of more than the algal growth rate. Within the surface mixed layer of a body of water, the algal growth rate (pnu, d-1) is the rate of supply of new algal biomass by means of cell growth and division, whereas grazing/death (g, d-1), sinking (s, d-1), and net advective/diffusive losses (a, d-1) influence the accumulation of algal biomass (B, mg *chlorophyll a* m-3)

$$dB/dt = B(pnu - g - s - a) \qquad \text{(eq. 3)}$$

The application of equation 3 may be viewed in the conceptual diagram shown in figure 4. In this simple parameterization of a segment or parcel of a surface mixed layer, the net advective/diffusive losses (a) are the sum of upstream input (+i, d-1) and downstream outflows (-o, d-1) within the surface mixed layer, upwelling from the bottom layer (+u, d-1), and downwelling into the bottom layer (-d, d-1). In a modeling exercise, s and d could be combined as a composite variable, but it is important to realize that the physical processes influencing s and d are different. Note that B also reflects only living algal biomass; detritus derived from living algal biomass should be parameterized separately. The sedimentation rate combines both the sinking rate of algal biomass (direct sinking of algal cells across the pycnocline) as well as a fraction of the grazing rate representing fecal pellets that sink across the pycnocline.

The accumulation of algal biomass over a time interval is the integral of equation 3. The value of the integral will depend upon the behavior of the variables that influence biomass. If the algal growth rate, pnu, is much larger than the other terms in equation 3, then pnu will dominate in the integration, and biomass will accumulate at a rate nearly equivalent to that of pnu. In this case, a nutrient limiting the algal growth rate also will limit the biomass accumulation rate in the segment. However, at the other extreme, if pnu is small or equivalent to the losses and advection/diffusion terms, biomass will accumulate only if it is

imported (e.g., from upstream or from bottom waters). In this case, biomass accumulation may be limited by a different nutrient than the one that limits growth rates in the local surface mixed layer. In this case, to understand the accumulation of algal biomass, nutrient limitation must be viewed on a larger scale of both time and space. An example is given below.

Management of an estuary such as Chesapeake Bay must be done at the largest temporal and spatial scales. This will be larger than the scale of an individual segment shown in figure 4, and the best choices for time and space scales are probably the largest ones at which the effects of eutrophication have been observed. Malone (1992) has shown that these scales in Chesapeake Bay are 1-3 months and 10-100 km for the mesohaline bay, but management of a large estuary such as the Chesapeake will probably have to occur at the full estuarine scale (seasons or years and hundreds of km). Edmondson (1991) provides an excellent example of how management at the basin scale is required to alleviate eutrophication in lakes.

3. Review of Nutrient Limitation in Aquatic Systems

In the rapid economic expansion following World War II, water quality was generally sacrificed in North America and Europe. Industries and cities expanded, suburbs flourished, and increased fertilizer applications led to greater crop yields per hectare. The result was increasing quantities of nutrients and other anthropogenic materials carried by streams and rivers into lakes, estuaries, and coastal seas. The resulting enrichment, or eutrophication, caused algal blooms, changes in trophic structure, fish kills, and anoxia in sensitive areas (Goda et al. 1991, Edmondson 1991, Mee 1992, Caddy 1993, Howarth 1993).

Since the 1960s, much research has been devoted to addressing these problems (e.g., Vollenweider 1976, U.S. Environmental Protection Agency 1982, Edmondson 1991). One of the more important goals has been to determine which nutrient has been the most limiting and hence most responsible for creating eutrophication. The objective has been to enable management to focus on controlling eutrophication by restricting the supply of the limiting nutrient or nutrients.

3.1 Experimental Methods to Detect Nutrient Limitation

There are several means of identifying limiting nutrients based on nutrient and particle concentrations (Table 1). Most of these tests assess growth rate limitation; however, several integrate over time and space scales larger than days/liters (particulate CNP, average , TN/TP), and ecosystem level responses based on biomass accumulation are also included.

An initial approach to assess growth rate limitation is to examine nutrient concentrations. There are two convenient reference points used to provide a scale for concentrations of dissolved inorganic nutrients(1) the analytical detection limit of a nutrient ([nutrient](sub dl)) and (2) the half-saturation constant for uptake (Knutrient). The values of Knutrient and [nutrient](sub dl) provide a scale with which to judge whether nutrient concentrations ([nutrient]) are high or low (e.g., Fisher et al. 1988). When, for example, [NO3] K(sub

NO3), NH4] K(sub NH4), or [PO4] K(sub PO4), the uptake rates of nitrate, ammonium, or phosphate are close to maximal, suggesting little N or P limitation. If [NH4]

There are large differences in the utility of this scale for N and P. Analytical detection limits for standard colorimetric analyses of NH4, NO2, and NO3 are typically an order of magnitude lower than the half-saturation constants for uptake (table 2). In contrast, [PO4](sub dl) is typically only 2-3 times smaller than K(sub PO4). Combined with questions of the biological availability of molybdate reactive PO4 under high biological demand (e.g., Lean 1973), this results in weak analytical ability to detect true [PO4] at low concentrations. For this reason, [PO4] (as estimated by soluble reactive PO4) is often only weakly related to other measures of nutrient uptake or limitation (e.g., Bradford and Peters 1987, Fisher et al. 1992b).

Nutrient ratios are also commonly used to infer nutrient limitation. One approach is to compare the molar ratios of dissolved inorganic nutrient concentrations to the biomass ratios of phytoplankton (Redfield 1958) an approach known as the Redfield ratio (CNSiP = 10616161)(e.g., Magnien et al. 1992). However, the use of the Redfield ratio is subject to the same limitations mentioned above for nutrient concentrations; when nutrient concentrations approach their detection limits, ratios of the nutrients are difficult to interpret.

Another approach is comparison of TNTP or particulate CNP ratios to the Redfield ratio (Hecky and Kilham 1988, Hecky et al. 1993). The limiting nutrient can then be inferred from deficiencies in N, P, or Si relative to carbon (C) or the other elements. The particulate ratio integrates the recent history of nutrient availability to the plankton, but assumes that the particulate matter is dominated by phytoplankton, which may not be reasonable in aquatic systems receiving large quantities of allocthonous organic matter. Particulate CNP ratios vary with nutrient deficiency because, as described above, phytoplankton have a large capacity to store P, but only a limited capacity to store N.

Nutrient addition bioassays have a long history in both fresh and marine waters (table 1). Potentially limiting nutrients are added singly and together to aliquots of a water sample, and the algal growth rate responses are compared relative to an unenriched control and the complete nutrient additions. Initially, a short term (2-6 h) response using 14C-CO2 following nutrient addition was used, but it was later shown (Healey 1979, Lean and Pick 1981) that inhibition of carbon dioxide (CO2) uptake frequently occurs following addition of the limiting nutrient as cells switch from reducing CO2 to uptake of the newly available limiting nutrient. Lean and Pick (1981) reviewed the literature on bioassays available at that time and recommended longer incubations to avoid this short-term competition for energy resources, as long as the unenriched control does not collapse because of extreme nutrient deficiency.

The pattern of response to nutrient additions can be used to indicate the nutrient that most limits short-term growth rates (Morris and Lewis 1988, Fisher et al. 1992a, 1992b). Nutrient addition bioassays are usually conducted on limited spatial and temporal scales (liters/m3, hours/days) and must be interpreted in terms of growth rates, as described above. However, at considerably greater expense and effort, nutrient addition bioassays may be done at larger spatial and temporal scales (mesocosms of 1-10 m3 volume and

week/month duration to multiyear efforts in whole lakes). Although smaller-scale measurements usually agree with ecosystem responses at the largest scales (Howarth 1988), this is not always true (Gerhart and Likens 1975, Schindler 1977, Hecky and Kilham 1988, Lean et al. 1989), primarily because it is impossible to anticipate and include all processes influencing the outcome of bioassays. However, the bioassay results obtained by Fisher et al. (1992a, 1992b) at small scales in the main stem of Chesapeake Bay (liters, days) were very similar to the mesocosm results (m3, weeks) reported by D Elia et al. (1986) and Webb (1988) in the Patuxent and York subestuaries of Chesapeake Bay.

Physiological expressions of nutrient limitation of growth have also been used in small-scale studies. For N limitation, CO2 uptake in the dark following addition of NH4 has been employed as an indicator of amino acid synthesis and N deficiency (e.g., Yentsch et al. 1977). The ratio of glutamine to glutamate in the internal amino acid pool has also been shown to be a useful indicator of N-depleted cells (Flynn et al. 1989, 1993, 1994, Flynn 1990). The ratio of carotenoids to chlorophyll a (Heath et al. 1990) and activity of cell-surface deaminases (Palenik and Morel 1990a, 1990b) have been shown to increase with N deficiency. Most of these were initially described using N-deficient cultures and only recently have been applied to field populations.

Physiological indices have also been developed for P limitation of growth rates, primarily for fresh waters. The activity of the cell-surface enzyme alkaline phosphatase is widely associated with P deficiency (see review by Cembella et al. 1984a). The turnover time of the ambient orthophosphate pool was first proposed by Lean and Nalewajko (1979) as a measure of P limitation that integrates the external availability of P, the internal storage of P, and cell biomass. Rapid turnover times of

Finally, at the ecosystem level, measurements of nutrient limitation of biomass accumulation have been made at large spatial and temporal scales. Nutrient budgets, correlations between nutrient inputs and algal biomass or annual primary productivity, and experimental manipulation of lakes have been used at this scale (table 1). Vollenweider (1976) and Vollenweider and Kerekes (1980) demonstrated clear correlations between nutrient loading and algal biomass in northern temperate lakes. However, correlations between nutrient inputs and algal parameters may be difficult to interpret because N, P, and Si inputs may be correlated with each other, and large fractions of the total nutrient load often enter together (e.g., Boynton et al. submitted). The most unambiguous results are obtained by direct experimental manipulations of whole ecosystems; those that have been done in lakes (e.g., Schindler 1977) were convincing demonstrations of the relative roles of C, N, and P in controlling algal biomass accumulation in northern temperate lakes. Nutrient limitation of biomass accumulation at the ecosystem level is more expensive to assess than the methods for growth rate limitation described above, but the results are the most relevant to the management of eutrophication.

3.2 Results of Experimental Measurements of Nutrient Limitation

Using combinations of these methods, two landmark papers published in Science in the 1970s established some clear principles concerning eutrophication. Whole-lake manipulations in the experimental lakes area of Ontario showed that northern temperate lakes evolved towards P limitation (Schindler 1977). When the lakes were fertilized with P,

N fixation and CO2 invasion from the atmosphere provided adequate C and N to balance P inputs. The result was that P limited both the growth rates and biomass accumulation of phytoplankton in these experimentally enriched lakes. Furthermore, Schindler (1977) hypothesizedthat the availability of C and N from the atmosphere might introduce time lags into lake responses. Lakes that had recently experienced a large P increase might temporarily show C or N growth limitation, but eventually CO2 invasion and N fixation would result in P limitation of biomass accumulation. Mechanisms that maintain P limitation have been identified as high NP loading, N fixation, and sediment retention of P in fresh waters (Howarth 1988, Caraco et al. 1990,Levine and Schindler 1992). As a result of this research, freshwater lake management has become firmly centered on control of P sources (Vollenweider and Kerekes 1980, Organization for Economic Cooperation and Development 1982). There have been many sucessful improvements in the water quality of temperate freshwater lakes as a result of P reductions (e.g., Boyce et al. 1987, Forsberg 1987, Lean et al. 1990, Edmondson 1991), and P fertilization of oligotrophic freshwater lakes has been used to improve fish yields (Stockner and Shortreed 1985). There is therefore both a firm experimental and practical basis for lake restoration through the use of P management.

The second landmark paper in Science was that of Ryther and Dunstan (1971). These authors examined the distributions of dissolved inorganic nitrogen (DIN) and PO4 in estuarine and coastal waters in the vicinity of Long Island and the New York Bight, and they conducted nutrient addition bioassays with cultures of phytoplankton that grew in those waters. Their results were as clear as those of Schindler (1977), but with the opposite conclusionthere was excess PO4 and depleted DIN in surface waters, PO4 was liberated more rapidly from decomposing organic matter than was NH4, and algae responded primarily to N additions in the bioassays.

As a result of this research, the concept of N limitation of phytoplankton in seawater became established among biological oceanographers. However, this is less widely accepted among chemical oceanographers and many policymakers (e.g., Smith 1984, Smith and Hollibaugh 1989). Subsequent marine research has identified the following mechanisms that tend to maintain N limitation of phytoplankton in seawaterenhanced sediment release of P relative to N (Nixon et al. 1980, Caraco et al. 1990), slow rates of N fixation (Howarth 1988, Howarth and Cole 1985), and high rates of denitrification (Seitzinger 1988). However, the experimental basis for N limitation of algal accumulation in seawater is less substantial than the case for P limitation in fresh water because only growth rate indicators have been used (Hecky and Kilham 1988, Howarth 1988, Vitousek and Howarth 1991, Hecky et al. 1993). Experimental manipulation at the ecosystem level is usually impractical in marine systems, and most experimental tests consist of small-scale bioassays showing response to N additions and observations of low DINPO4 compared to the Redfield ratio of 161 (Redfield 1958). However, the few larger-scale experimental tests of nutrient limitation that have been done in estuarine and marine systems (D Elia et al. 1986, Webb 1988, Vitousek and Howarth 1991) have provided evidence supporting the occurrence of N limitation. In addition, there is at least one successful example of management based solely on the control of N inputs to eutrophied marine waters (Johansson and Lewis 1992).

Continued research in the 15-20 years since the establishment of these concepts has blurred

the simplicity and clarity of the original ideas. Several recent reviews (McCauley et al. 1989, Prairie et al. 1989, Elser et al. 1990) and many individual reports (e.g., Setaro and Melack 1984, Goldman 1988, Morris and Lewis 1988, Dodds and Priscu 1990) have concluded that N may at times be important in controlling the algal biomass of lakes. It is also recognized that N can control the taxonomic composition of algal biomass in temperate lakes, as when N-fixing cyanobacteria form nuisance blooms in temperate lakes under N-depleted conditions in summer, and this is often one of the most objectionable consequences of eutrophication (e.g., Edmondson 1991).

In marine waters, other elements may also limit growth rates and biomass accumulation. There are reports of P limitation of phytoplankton, macroalgae, and macrophytes, particularly in tropical waters with calcareous sediments that can bind PO4 (Short et al. 1985, 1990, LaPointe et al. 1992, Harrison et al. 1990, Capone and Dennison 1994). It has been proposed that the availability of dissolved iron (Fe) regulates the abundance of phytoplankton in large regions of the high temperate and polar oceans (Martin and Fitzwater 1988, Martin et al. 1989, 1990), but there is considerable controversy with regard to this concept (Banse 1990, Dugdale and Wilkerson 1990, Peng and Broecker 1991). It is also clear that the original work by Ryther and Dunstan (1971) was carried out in waters heavily influenced by sewage from New York City (e.g., Simpson et al. 1975), and that the results of Ryther and Dunstan (1971) may not be representative of marine waters in general.

How widespread is N limitation in marine waters? In a broad overview of terrestrial and aquatic systems, Vitousek and Howarth (1991) reviewed how N limitation can occur on land and in the sea. With abundant N2 present in air and water, why isn t N fixation moreimportant in temperate forests and marine systems? Vitousek and Howarth (1991) examined several hypotheses and presented a list of potential biogeochemical mechanisms that favor nitrogen limitation, including the high mobility of nitrate, the energetic importance of denitrification, differential recycling of N and P, and limitation of N-fixing organisms by another element (molybdenum, Fe, or P) or by grazing. Although the relative importance of these mechanisms is unknown, the authors concluded that N limitation of net primary production (biomass accumulation) is widespread but not exclusive in most terrestrial biomes and many marine systems.

Given this degree of uncertainty in the scientific understanding of nutrient limitation in fresh waters and seawater, it was unlikely that a simple paradigm would emerge from estuarine research on nutrient limitation. In estuaries and coastal ponds, which are seasonally varying mixtures of fresh water and seawater, there is considerable evidence for seasonal and spatial variations in the limitation of phytoplankton growth and abundance by light, P, and N (McComb et al. 1981, Myers and Iverson 1981, D Elia et al. 1986, Caraco et al. 1987, Caraco 1988, Webb 1988, Fisher et al. 1992a, 1992b). For example, in the Patuxent and York subestuaries of Chesapeake Bay, meso-scale bioassays indicated P limitation of biomass accumulation during winter and spring with high river inflows and N limitation during summer with lower river flow (D Elia et al. 1986, Webb 1988). Fisher et al. (1992a, 1992b) also presented evidence from bioassays (1-3 days each) for similar seasonal alternations in P and N limitation of algal growth rates in the mainstem of the Chesapeake and its tributaries. These reports suggest that estuaries may act like

freshwater lakes in winter and spring under strong riverine influence, but more like enclosed marine basins in summer and fall under a stronger oceanic influence.Other estuaries such as Delaware Bay (Sharp et al. 1982, Pennock 1985, Lebo and Sharp 1992), the Hudson River estuary (Malone 1977, Malone et al. 1980, Cole et al. 1992), and San Francisco Bay (Cloern 1987, Fisher et al. 1994) are more turbid and well mixed than Chesapeake Bay, and have excess nutrients (Knutrient) for much of the year except when phytoplankton blooms form under favorable hydrologic conditions. These turbid and well-mixed estuaries appear to be light limited for substantial parts of the year. Thus there is evidence for strong seasonal and spatial variations in light, N, and P limitation of phytoplankton growth and accumulation in estuaries. The productivity and accumulation of algal biomass do not appear to be limited by a single resource within these complex mixtures of fresh water and seawater.

4. Nutrient Limitation and Estuarine Structure

This section explores seasonal and spatial variations in nutrient limitation and the influence of estuarine circulation on nutrient limitation. It takes Chesapeake Bay as a primary example of eutrophication, degraded water quality, and reduced fisheries yields over the last 50 years (Harding 1994, U.S. Environmental Protection Agency 1982). Appropriate scaling is especially important in assessing nutrient limitation in estuaries because of the inherent spatial and temporal variability.

Algal growth and accumulation are influenced by the circulation patterns in estuaries. In the case of Chesapeake Bay, light limitation occurs in the northern, oligohaline regions (Harding et al. 1986). The high nutrients, turbidity, and depth of mixing in the Susquehanna River water result in light limitation as the river flows into the estuary; furthermore, once the river water enters the Bay and begins to mix with salt water, particulates carried by the river flocculate and sink into the bottom layer (Schubel 1968, Meade 1968, Zabawa 1978, Eisma 1986). Once on the bottom, they are resuspended by tides (Schubel 1968) and transported in a landward direction by the net nontidal flow (see figure 5). The countercurrent circulation conserves and concentrates the particles into a turbidity maximum, and the reduced turbulence in the stratified region of the turbidity maximum results in an accumulation of deposits on the bottom (Meade 1968, Peterson et al. 1975, Geyer 1993). Within the turbidity maximum, algal biomass may decline because of greater shading and salinity changes (Cloern 1987). The location of the turbidity maximum moves seaward with increasing river flow (Peterson et al. 1975, Festa and Hansen 1978), and the turbidity maximum in Chesapeake Bay is usually restricted to the northern region between the Chesapeake Bay

Bridge and the mouth of the Susquehanna River (Schubel 1968, Fisher et al. 1988).

A chlorophyll maximum is a second estuarine feature influencing nutrient limitation in estuaries. In Chesapeake Bay, downstream from the turbidity maximum, the water column clears in surface waters, algae accumulate, and nutrients decline by algal uptake and by dilution with low-nutrient seawater (Harding et al. 1986, Malone et al. 1988, Fisher et al. 1988). Like the turbidity maximum, this biologically active region the chlorophyll maximum (Harding et al. 1986, Fisher et al. 1988) responds to hydrology, moving seaward under high flows and staying downstream of the turbidity maximum. In shallow estuaries such as San Francisco Bay, the chlorophyll maximum may co-occur with the turbidity maximum under certain flow regimes because the depth of mixing is physically constrained (Peterson et al. 1975, Cloern et al. 1985, Moon and Dunstan 1990). In turbid and well-mixed Delaware Bay, chlorophyll maxima primarily occur in the lower bay during spring runoff when there is sufficient density stratification to limit tidal and wind mixing (Pennock 1985, Fisher et al. 1988). The chlorophyll maximum in the Hudson River estuary primarily occurs in the shelf waters after the turbid, nutrient-rich water is discharged beyond the enclosed portion of the Hudson (Malone et al. 1980).

In Chesapeake Bay, the development of a chlorophyll maximum results in nutrient consumption. The chlorophyll maximum develops within the zone of clearing water downstream from the turbidity maximum, and nutrient concentrations decline downstream as a result of nutrient consumption and dilution with seawater.Figure 6,based on data from April 1983, shows the distribution of surface water characteristics in Chesapeake Bay from the Susquehanna River at the northern, freshwater end of the bay to the estuarine plume out onto the continental shelf south of Cape Henry. At that time, salinity increased down the length of the bay, and the turbidity maximum was present in the upper bay, north of the Chesapeake Bay Bridge. There were 20 optical depths in the surface mixed layer at the turbidity maximum, indicating light limitation of algal growth (Harding et al. 1986). Downstream of the turbidity maximum, in the vicinity of the bridge, a primary chlorophyll maximum developed with table 2). DIN and SiO4 were present in excess in the primary chlorophyll maximum (both 5 microM [0.07 mg DIN and 0.14 mg SiO4-Si l-1]). Exhaustion of the riverine PO4 probably limited the development of further algal accumulation in the primary chlorophyll maximum, in that there were

There was also a secondary chlorophyll maximum in this April 1983 example. The secondary maximum was present in a broad area centered near the mouth of the Potomac River, and it was associated with PO4 and SiO4 depletion and a continued excess of DIN. At the southern end of the bay, near the James and York Rivers and out into the plume on the shelf, chlorophyll declined, DIN was depleted to levels of

All three major plant nutrients are depleted sequentially along the length of the Bay in this spring example. PO4 was the first nutrient to be depleted and was present at low concentrations over the longest length of the bay (~230 km). SiO4 was depleted next over an intermediate length of thebay (~120 km), and DIN was depleted last over the shortest length (~40 km).

Which nutrient limited phytoplankton biomass accumulation in the Bay as a whole in this example? It is possible to develop arguments supporting each element as the primary limiting nutrient, but within the conceptual models developed above, this kind of evidence suggests that the supply of riverine PO4 limited the local development of the primary chlorophll maximum, that the secondary chlorophyll maximum in the middle of the Bay (probably composed of diatoms) may have been limited by the supply of SiO4 and PO4 (from multiple sources), and that riverine DIN may have set a limit for algal biomass at the seaward end of the estuary, although all three nutrients were at trace levels. The residual PO4 concentrations in the more saline areas were probably maintained by local regeneration processes, but the secondary chlorophyll maximum must have developed from a secondary supply of PO4, perhaps derived from the Patuxent River, Potomac River, or net seawater inflows in bottom waters.

This example illustrates the difficulty in managing Chesapeake Bay. Which nutrient should be controlled to reduce biomass accumulation and the organic matter supply for development of anoxia? This question is the central issue addressed by this paper.

Figure 7 summarizes the estuarine structure and processes discussed above. It shows a vertical supply of organic matter from local surface waters, which, in the April 1983 example of the primary chlorophyll maximum in figure 6 , was probably limited by the P supply from the Susquehanna River. The vertical supply of organic matter from the secondary chlorophyll maximum was probably limited by Si and P from both freshwater and seawater sources. In contrast, the horizontal supply of organic matter transported in the subpycnocline flow in figure 7 is derived from cumulative sedimentation

resulting from production within the entire estuary. The net effect is up-bay transport of particulate or dissolved organic matter and/or bottom waters with increasingly low dissolved oxygen. This cumulative internal source is probably determined by the supply of N from freshwater inputs, in that this element is supplied primarily from freshwater, unlike P (e.g., figure 6). The key to answering the question posed above is the relative importance of local sedimentation and estuarine transport in supplying organic matter to bottom waters, in that the availability of organic matter for each transport process appears to be limited by different elements. However, there do not appear to be any studies on the relative importance of local sedimentation and the estuarine circulation in supplying algal biomass to bottom waters. The relative importance of these two processes undoubtedly varies temporally and spatially within each estuary, and it is recommended that studies be undertaken on the relative importance of sedimentation and subpycnocline transport of algal biomass.

The above analysis suggests that there are two major time and space scales that are important for nutrient limitation and development of anoxia in estuaries. First, local nutrient limitation of surface waters determines the local vertical flux of organic matter to bottom waters. The time and space scales for local nutrient limitation are determined by the local residence time of surface waters within the average tidal excursion, on the order of 1-10 days and 5-10 km. Second, nutrient limitation of surface waters in the estuarine system as a whole determines the horizontal advective flux of organic matter by way of subpycnocline transport. The time and space scales for the Chesapeake as a system are much larger and again related to the water residence time, on the order of 3-6 months and 100-200 km.

The role of N and P in the development of anoxia in Chesapeake Bay depends on the relative importance of the delivery of organic matter to bottom waters by vertical and horizontal fluxes (see figure 7). These fluxes are controlled by local- and estuarine-scale nutrient limitation, which, in the April 1983 example shown in figure 7, were P and Si (depending on location) and N, respectively. Investigation of the relative importance of the vertical and horizontal fluxes of organic matter to bottom waters is thus of considerable concern for the environmental management of Chesapeake Bay in general and for the control of anoxia in the Bay in particular.

5. Experimental Studies of Nutrient Limitation in Chesapeake Bay

As stated above in general terms, there is evidence for seasonal and spatial

variations in light, P, and N limitation of phytoplankton growth in Chesapeake Bay (D Elia et al. 1986, Webb 1988, Fisher et al. 1992a, 1992b). This section presents summaries of the experimental evidence from field studies of nutrient limitation, including nutrient addition bioassays and nutrient turnover measurements. The following section presents similar evidence from modeling studies.

5.1 Nutrient Addition Bioassays

The nutrient most limiting algal growth is often determined in nutrient addition bioassays (table 1). Using uniform subsamples from a station, N, P, and Si are added singly and together, usually as NH4 or NO3, PO4, and SiO4. Controls with no additions and experimental treatments are incubated for one to several days, and the limiting nutrient is determined from the pattern of experimental stimulation of algal growth rates, which is usually measured as chlorophyll a and/or 14C-CO2 uptake. Details of the procedures, statistics, and interpretation of nutrient addition bioassays can be found in Fisher et al. (1992a, 1992b).

There have been several studies in the Chesapeake that have used nutrient addition bioassays (table 3). In addition to the mesoscale studies of D Elia et al. (1986) and Webb (1988) mentioned above, Fisher et al. (1992a) used 24 h incubations on a ship at five stations along the mainstem of Chesapeake Bay, and Coley et al. (1990) used a similar protocol at three stations along the length of the bay in a program on land margin ecosystem research (LMER) funded by the National Science Foundation. In an extensive study funded by the Maryland Department of the Environment, Fisher et al. (1992b) employed bioassays at ten stations in Maryland waters of Chesapeake Bay over a two year period to assess nutrient limitation of phytoplankton growth. In a parallel study funded by the Virginia Coastal Resources Management Program, Haas and Wetzel (1993) employed similar bioassays at six stations in Virginia waters of the bay over a one year period.

A detailed example of bioassay results is shown in figures 8a-c from a mainstem station just south of the Choptank River (data from Fisher et al. 1992b). This station (monitoring station MCB4.3C, LMER station BM7) is located at ~km 175 in figure 6, in the area in which seasonal chlorophyll maxima are found. The lower panel of figure 8a illustrates monthly variations in nutrient concentrations in surface waters between August 1990 and June 1992. There were winter maxima of DIN (NH4+ NO2 + NO3 = DIN) and SiO4 resulting from seasonally high river flow; concentrations exceeded 20 microM

(0.28 mg DIN l-1 and 0.56 mg SiO4-Si l-1) at this time of year. However, PO4 was nearly continuously at low concentrations (

Bioassay growth responses are shown in figure 8b. Changes in the growth rate were measured relative to a control 24-72 h following separate and combined additions of NH4, PO4, and SiO4 (30 microM, 2 microM, and 30 microM, respectively [equivalent to 0.42 mg DIN l-1, 0.062 mg PO4-P l-1, and 0.84 mg SiO4-Si l-1]). The length of the incubations varied with ambient water temperature and light levels to provide a constant potential for growth responses (at least two doublings). The dotted lines in figure 8b are threshholds for significant responses developed from analysis of maximum growth responses at different seasons (see Vaas and Magnien 1992, Fisher et al. 1992b). Growth rate responses (average percent increases in chlorophyll a and 14C-CO2 incorporation) in excess of these lines are considered to be significantly enhanced relative to the control (no additions). The complete additions (+NP, +NPSi) usually elicted the largest increases in growth rate, occasionally exceeding 1000% relative to the control (10-fold increase; see upper panel of figure 8b). This provides strong evidence for the restriction of algal growth rates by the availability of nutrients. Within the individual additions (lower panel of figure 8b), SiO4 elicited no significant responses; however, there were significant responses to PO4 from March through June, when DIN was available in excess (figure 8a). These results have been interpreted as indicative of primary and exclusive P limitation of algal growth rates (see table 4 and figure 9 for definitions of bioassay classifications). As shown in figure 8b, NH4 stimulated growth from June through September, principally when DIN was depleted (figure 8a). These results have been interpreted as indicative of primary and exclusive N limitation of algal growth rates. Note the lack of significant responses to nutrient additions, single or combined, from November through February in figure 8b. These results have been interpreted as light limitation and occur when DINand SiO4 are high; typically, there is growth in the control and all treatments regardless of additions (all samples are maintained at 60% of ambient light). The data in figure 8b provide detailed information on sequential limitation of phytoplankton growth rates by light, P, and N during winter, spring, and summer/fall in the region of Chesapeake Bay in which chlorophyll maxima form.

An index of P deficiency has also been calculated from the bioassay data (figure 8c). The index was calculated using the increase in particulate P (PP) following nutrient additions, relative to the control, and reflects both biomass accumulation and replenishment of intracellular P stores (see figure 3 and

table 4). N and Si treatments elicited a response in PP only if biomass accumulation occurred with additions of PO4 from external pools; however, significant increases in PP were rarely observed in the +N and +Si treatments, even when N was the primary limiting element in summer and fall (e.g., compare July/August 1991 data in figures 8b and 8c). This observation indicates little available external PO4, which is consistent with the low concentrations shown in figure 8a, and suggests that the enhanced growth rates in summer in N treatments occur by the mobilization of internal P stores (see figure 3).

In contrast, P additions usually elicited an increase in the PP parameter. Replenishment of internal P pools in +P treatments (single or combined) may occur if internal pools are unfilled even in winter under light limitation or at any time of year if growth occurs under N limitation. Significant PP responses were observed in the +P treatment during most months, except in July and August of 1991, following severe DIN depletion and a slight accumulation of external PO4 (figure 8a). This observation suggests that a source of PO4 became available that was largely consumed by the plankton to fill intracellular stores, but little accumulation remained in extracellar pools in surface waters. Subpycnocline anoxia and the diagenetic release of PO4 from sediments is a likely candidate for this source of PO4 at this time of year (Boynton and Kemp 1985).

The largest responses in the PP parameter in +P treatments were observed in spring. Very large increases in the PP pool (300% in 1-3 days) were observed during spring when P clearly limited algal growth rates and intracellular P stores were depleted (figures 8b and c). In general, the data of figure 8c show that internal P pools were rarely filled at this station, even when N and light were the primary limiting resources. This finding is consistent with the low extracellular PO4 (figure 8a) and the conceptual models described in figure 3 and table 3 and suggests that continuous biological uptake of PO4 (even under N or light limitation) is responsible for the low and stable PO4 concentrations observed in Chesapeake Bay (e.g., figures 6 and 8a).

The data in figures 8a-c show a complex pattern of resource limitation of algal growth rates. There was light limitation of growth rates in winter, P limitation in spring, and N limitation in summer and fall at this station. Furthermore, there were nearly continuous depletion of PO4 concentrations and partial depletion of internal P stores, even when light or N were the primary limiting resources. Note that these data were obtained at the smaller of the two scales (5-10 km, 1-10 d) that are being considered here. Although some grazing may

have occurred during the bioassays, most of the processes shown in figure 4 were excluded.

Results such as those shown in figure 8b have been used to compute indices of N, P, and light limitation of algal growth rates in the main stem of Chesapeake Bay. The present paper uses bioassay data for the years 1989-92 reported by Coley et al. (1990), Fisher et al. (1992b), and Haas and Wetzel (1993) from five stations in the main bay downstream of the normal position of the turbidity maximumMCB3.3C, MCB4.3C (LMER station BM7), MCB5.2, CB6.1, CB6.4 (LMER station S3). The first three stations are in Maryland waters; the other two are in Virginia waters. Bioassays that did not fit the patterns in figure 9 (11 out of 150 bioassays during 1989-92) have been excluded. The indices were calculated by weighting the classification of each bioassay response as shown in table 5. This weighting scheme gives greater weight to an exclusive N or P response than to a primary N or P or balanced NP, and it makes possible the averaging of responses over multiple stations to compute a baywide index. Each index runs from 0 to 1 and is equivalent to the fractional control that N, P, or light exerts over growth rates of algae. An index 0.5 for N, P, or light indicates that the resource exerts dominant control over growth rates.

These indices provide clear evidence of a seasonal progression in the dominance of light, P, and N in the control of algal growth rates along the main stem of Chesapeake Bay (figure 10). During winter (November-March) of each year during 1989-92, the light index (middle panel) was >= 0.5 for at least one month of this season, and was usually >= 0.5 in December through February. During spring (April-June) the P index (lower panel) was >= 0.5 in at least one month each year, usually peaking in May (except in 1989 as noted below). During the summer and fall (July-October), the N index was usually >= 0.5, peaking in August or September. In 1991 and 1992, there was a tendency for P limitation to return in late fall before light limitation became dominant in winter.

Figure 10 shows that light, N, and P did not consistently control algal growth rates during the four-year period. Each resource was important for several months at different times of the year. Furthermore, in these data from the main axis of the Bay, there is stronger evidence for spring and fall P limitation than in the mesocosms used in the Patuxent and York Rivers by D Elia et al. (1986) and Webb (1988). This observation is not the result of differences in bioassay scales (table 1), because Fisher et al. (1992b) and Haas and Wetzel (1993) also reported weaker spring P limitation in tributaries. Greater sewage inputs per unit volume in the tributaries may reduce the severity of spring P

limitation (see Fisher et al. 1992a).

In 1989-92, there was considerable interannual variability (figure 10), which appears to have been related to Susquehanna River hydrology. The year 1989 was anomalous, as noted above, because of an unusual spring discharge (upper panel of figure 10). Runoff from the Susquehanna River peaked in May, with greater discharge occurring two months later than normal and resulting in high turbidity in the Bay (Harding 1994) and a high index of light limitation through May (middle panel of figure 10). Furthermore, P limitation occurred throughout the summer, particularly in the upper Bay, and the N index exceeded 0.5 only in September. Harding (1994) has also noted the anomalous runoff, nutrient, and biomass patterns in 1989 in his review of 40 years of nutrient and chlorophyll a data in Chesapeake Bay. Bioassay data for 1990 are too sparse to compare with those of other years or with river hydrology, but in the winter of 1990-91 the prolonged high flows resulted in a high index of light limitation from November through February. In contrast, the relatively dry winter of 1991-92 apparently created little turbidity and resulted in a high index of light limitation only in December and January. These data suggest that the combination of low temperatures, low light, and turbidity derived from runoff result in light limitation of algal growth in large portions of the Bay during winter. Furthermore, unusually wet spring periods appear to delay the onset of P limitation from spring into summer and N limitation from summer into fall, probably because of the large inputs of turbidity and DIN.

There was also spatial variability in the Bay in the responses to nutrient additions. The only year with nearly complete data at all five main-bay stations to illustrate spatial differences is 1992; both Fisher et al. (1992b) and Haas and Wetzel (1993) reported main-bay bioassays for each month at five stations in the Virginia and Maryland portions of the Bay. However, there were missing data at the Virginia stations in January and December 1992 in Haas and Wetzel (1993), and their main-bay data from the same stations for January 1993 were used in place of the missing data. Classified monthly responses in the bioassays using the combined data sets for 1992 are grouped in figure 11 to illustrate the distribution of resource limitation in time and space.

In the winter of 1992 there was Baywide light limitation of growth rates. In January, all stations had no response to added nutrients (NOR in figure 11), which was interpreted as light limitation. Later, in February, in Virginia waters of the Bay, balanced NP (BNP) or primary N limitation (PRN)

occurred. However, in Maryland waters, nutrient limitation began in March, and algal growth rates were P limited, either primary P (PRP) or exclusive P limitation (EXP). Therefore, both the timing of the onset and type of nutrient limitation varied along the mainstem of the Bay.

The spring period of 1992 was characterized by P limitation of growth rates throughout the Bay. Primary P limitation and exclusive P limitation became widespread by May, even at the most southern station in Virginia waters nearest the ocean (station CB6.4). P limitation was brief at the southern end of the Bay (~1 month), and increased in duration up the axis of the bay to ~3 months.

The transition from spring P to summer N limitation occurred in June. In Maryland waters, there was a brief period of balanced NP limitation, whereas in Virginia waters the transition from primary P to primary N limitation occurred in

There was considerable spatial variation in responses in the fall. The southern Bay remained primarily N limited through November, but in Maryland waters there was a transition from N to balanced NP or primary P limitation in October. However, by December, most stations were light limited, except for one exclusive P response in the northern Bay at station MCB4.3C.

The data in figure 11 enable the following four conclusions to be drawn concerning spatial variations of resource limitation in 1992. First, the duration of winter light limitation was about a month longer in Maryland waters than in Virginia waters. Second, the duration of P limitation (EXP {BNP) was 1-3 months in Virginia waters and was primarily confined to the spring; however, in Maryland waters the duration of P limitation was 3 months in the spring and 2-3 months in the fall. Third, the entire bay was nearly uniformly limited by N (BNP {EXN) in the warm summer months. And finally, Virginia waters remained N limited through the fall, whereas Maryland waters shifted to P limitation in the late fall before the transition to winter light limitation. Ninteen ninety-two is the only year with sufficient temporal and spatial sampling to examine an annual cycle of spatial variations along the length of Chesapeake Bay; interannual variations and the effects of varying river hydrology are unavailable. These are likely to be large, and 1992 had a relatively dry winter/spring freshet compared to the previous 3 years (figure 10). It is suggested that further investigation of the spatial variation in resource limitation is a second area of considerable importance for the environmental management of Chesapeake Bay (in addition to the relative

roles of local sedimentation and estuarine transport).

The responses in the nutrient addition bioassays can also be related to ambient concentrations of N and P. The present paper uses the combined data of Coley et al. (1990), Fisher et al. (1992b), and Haas and Wetzel (1993) from the same five mainstem Chesapeake Bay stations to examine the relationship between bioassay results and concentrations and ratios of inorganic N and P. Figure 12 shows the relationship between the indices computed for bioassays run on water samples with ambient DIN in several ranges in 1989-92. Although the most common concentration of DIN in the mainstem of the Bay (particularly in Maryland waters) was >= 10 microM (0.14 mg l-1; top, left panel of figure 12), DIN-depleted samples were common in summer and fall throughout the Bay and were very common throughout most of the year in Virginia waters. In samples with 0.5), with DIN concentrations of 5-10 microM (0.07-0.14 mg l-1) indicating that N limitation is likely (N index = 0.4-0.5), and DIN concentrations >= 10microM (0.14 mg l-1) suggesting that N limitation is not likely (N index <0.2). The P and light indices increased gradually as DIN concentration increased to >= 10 microM, but neither individually exceeded 0.5 (right panels of figure 12).

The relationship of the bioassays to PO4 concentrations is shown in figure 13. In contrast to DIN, the most common PO4 concentrations at the main-stem Chesapeake Bay stations were <0.2 microM (figure 13 ; see also figure 8a). However, bioassays of these samples had a P index of

The relationship of the bioassays to the molar ratio of DIN/PO4 is shown in figure 14. There was a relatively uniform distribution of samples over the entire range of DIN/PO4 in this data set (upper left panel of figure 14), and there were ranges over which N or P indices were primarily >= 0.5. The N index was primarily >= 0.5 over the lower range of DIN/PO4 of 0-401; the P index was ~0.5 over the high range of DIN/PO4 of >= 1601; and all three indices were ~0.3 in the middle range of DIN/PO4 between 401 and 1601. Note that these ratios are higher than the NP ratio of 161 for average planktonic biomass (Redfield 1958); however, the association of DIN/PO4 ratios <641 (Smith 1983). These external ratios differ from biomass ratios because of the effects of internal P stores (figure 3) and the poor predictive ability of external PO4 concentrations (figure 13). Therefore, the atomic DIN/PO4 is a weaker predictor of nutrient limitation in mainstem Bay waters than is DIN concentration. However, values of DIN/PO4

5.2 Nutrient Turnover Studies

Nutrient turnover times obtained with isotopes are often used to indicate nutrient limitation (Lean et al. 1987, 1989). In limnology, a turnover time of the PO4 pool

Turnover times of the external PO4 pool were measured on LMER cruises at three stations in Chesapeake Bay between 1989 and 1993. The three stations are N3 (LMER North Bay process station, equivalent to MCB2.2), BM7 (LMER Mid Bay process station, equivalent to MCB4.3C), and S3 (LMER South Bay process station, equivalent to CB6.4). The turnover times of external PO4 were derived from 32P-PO4 measurements (Fisher and Lean 1992), and the seasonal distribution of turnover times are shown in figure 15 .

In the northern Bay (station N3), turnover times were long (generally 600 minutes or 10 hours), irrespective of month or year. This observation suggests no P limitation at any time of year at this station, and Coley et al. (1990) observed no responses to nutrient additions at this station.

In the middle of the Bay (station BM7), turnover times of external PO4 were usually shorter than in the northern Bay. Turnover times 60 minutes. The PO4 turnover times at this station suggest P limitation in the warmer months in the middle of the Bay, and much less P demand relative to supply in winter. This pattern is similar to the patterns shown in figure 10 and 11, except that P turnover times appear to be shortest in the middle of the Bay when bioassays suggest N limitation of growth rate.

In the southern Bay (station S3), PO4 turnover times fell into two general categories 60 minutes. In most years there was at least one value of PO4 turnover time <= 10 minutes in April through June. In the wet years 1989 and 1993, turnover times were also <= 10 minutes in July, whereas in 1992 the shortest turnover time was 19 minutes in April (there were no May or June data on turnover time in 1992). The turnover time data suggest that there is at least one month in late spring or early summer when P limitation of growth rates occurs in the southern end of Chesapeake Bay. However, with the exception of the wet years 1989 and 1993, PO4 turnover times in the southern Bay were usually 60 minutes for most of the summer and fall, implying less P limitation at this time of year. This pattern of apparent P limitation inferred from turnover times in the lower panel of figure 15 supports the temporal and spatial patterns of bioassay results shown in figures. 10 and 11.

6. Modeling Studies of Nutrient Limitation in Chesapeake Bay

Empirical data for seasonal changes in light, P, and N limitation of algal growth rates in Chesapeake Bay, as summarized above, are critical for understanding the complex and dynamic processes that occur in the Bay. However, there is also a need for management and diagnostic tools at the estuarine scale to implement a basinwide strategy of nutrient reduction. An agreement implementing such a strategy was signed by Pennsylvania, Maryland, Virginia, the District of Columbia, the Chesapeake Bay Commission, and U.S. Environmental Protection Agency in 1983 and was expanded in 1987.

Controlling N and P has been the primary strategy for water quality improvements in the Bay and its tributaries. Some reductions have been made in P inputs, but N inputs have increased (Boynton et al. submitted). The evidence shown above clearly supports the need to reduce inputs of both N and P to control algal growth rates in the Bay (e.g., figures 10 and 11). However, estuarine-scale (ecosystem) decreases in biomass in response to future N and P reductions may not be predicted well by growth rate data because other processes besides growth control biomass accumulation (see figure 4). The following is an attempt to address this problem by using the Chesapeake Bay Water Quality Model. This model has been calibrated with monitoring data and used to simulate estuarine-scale responses to reductions in nutrient inputs from the watershed. Results from these model runs are being used to evaluate various approaches to nutrient reduction strategies in the Chesapeake Bay watershed (Butt 1992).

6.1 Chesapeake Bay Water Quality Model

The Chesapeake Bay Water Quality Model, referred to as the 3D model, is composed of three separate models. Each one is designed to represent key components that make up the dynamics of the Bay and its watershed. The watershed model (Donigian et al. 1991) estimates nutrient loads from the Bay s 160,000 km2 of drainage area. Output from this model is used as input to the water quality model, which simulates the Bay s response to river flow and nutrient inputs. The hydrodynamic model, modified from Sheng (1983, 1984) for use on Chesapeake Bay by Johnson et al. (1991) and Dortch (1990), simulates the currents, temperature, and salinity regimes of the Bay. The nutrient components of the water quality model are driven by physical processes as well as by input from a sediment submodel (DiToro and Fitzpatrick 1993). The output of the water quality model are the chemical and biological constituents of the water column (Cerco and Cole 1994). In the model runs reported here, results from various nutrient reduction strategies

were evaluated for the entire Bay at large temporal and spatial scales, i.e., the estuarine scale (as described above; see Butt 1992 for a complete description).

Scenarios were generated to cover a wide range of nutrient load conditions. The model was calibrated using 1984-86 data from the Chesapeake Bay monitoring programs. This effort established the baseline conditions against which load reductions were compared (scenario 1 base case). Model results were averaged with both temporal and spatial aggregation within nine geographic zones of the Bay (figure 16). Aggregation by season was based on winter as January-February (Julian days 1-60, up to the onset of the spring bloom), spring as March-May (Julian days 61-150, up to the end of the spring bloom and the onset of anoxia), summer as June-September (Julian days 151-270, up to the fall overturn), and fall as October-December (Julian days 271-365).

Both horizontal and vertical aggregation were used to integrate properties within the geographic zones of the Bay (Cerco and Cole 1994). The values associated with cells (see figure 16) were integrated horizontally over each zone and vertically over depth within the surface mixed layer to the pycnocline (approximately 6 m). Similar integrations were performed over the bottom layer of the water column, which extended from the pycnocline to the topographically varying bottom. Algal biomass and productivity were integrated by season and zone over the surface mixed layer only, whereas model results for dissolved oxygen were integrated vertically and laterally across each row of cells within the bottom layer to show more detailed distributions. The data reported below were plotted at the geographic midpoint of each zone or row of cells along the Bay s longitudinal axis.

Although the first scenario was calibrated under existing conditions, the second scenario reduced inputs of both N and P to the limit of technology (LOT NP). This established the upper boundary of practical load reductions using a combination of point source controls at the limit of technology and the most comprehensive best management practices for diffuse sources in the three states of the Chesapeake Bay Agreement. Point source effluent from municipal facilities was held to 3.0 mg N l-1 (210 microM N) and 0.075 mg P l-1 (2.4 microM P), compared to typical total N and P concentrations of 12 mg N l-1 (870 microM N) and 3.7 mg P l-1 (120 microM P) in sewage after secondary treatment (Fisher et al. 1992a). Overall, application of LOT NP methods reduced projected N and P inputs by 20-30% and 35-55%, respectively.

The third and fourth scenarios explored N and P reductions separately. In the third scenario (LOT N), P loads were held at base-case conditions, but N controls were applied for point and diffuse sources at the limits of technology in the three states. In the fourth scenario (LOT P), N loads were held at base-case conditions, but the above P controls were applied for point and diffuse sources.

6.2 Base-Case Simulation of Phytoplankton Biomass and Productivity

A critical test of modeling studies is the ability to reproduce observed ecosystem properties. Following are brief reviews of oceanographic measurements of algal biomass and productivity for comparison with 3D model simulations of base-case conditions. These are provided to show that the model adequately meets this criterion in the base-case simulation.

Oceanographic studies have shown that maxima of phytoplankton productivity and biomass in Chesapeake Bay occur at different seasons. Although phytoplankton productivity is moderate in spring, biomass accumulation is greatest in late spring because grazing and other losses are low. Biomass accumulates in surface and bottom waters prior to the onset of anoxia (Malone et al. 1988, White and Roman 1992). Although biomass accumulation is greatest in spring, peak seasonal phytoplankton productivity occurs in summer in Chesapeake Bay (Harding et al. 1986, Malone et al. 1988), as in many other estuaries (Fisher et al. 1982). However, summer biomass accumulation is moderate because of grazing and other losses. Therefore, seasonal peaks in growth-based productivity (summer) do not coincide with maximal biomass accumulation (spring). This is the result of the need to consider processes other than growth at the larger time and space scales associated with biomass accumulation, as described above (in the text and in figure 4).

Chesapeake Bay model results sucessfully reproduced these field observations under base-case conditions. In the model output, peak biomass occurred in spring (figure 17A), and peak primary productivity occurred in the summer (figure 17B). The spatial gradient in biomass was greatest in the spring, when biomass peaked at ~0.17 g chlorophyll a m-2 in the middle of the Bay, about 100-200 km from the Bay's mouth. This corresponds to the location of the observed maxima of volumetric chlorophyll a shown in figure 6, and the biomass levels agree very well with those reported by Harding et al. (1986) and Malone et al. (1988) for surface mixed layers and euphotic zones, respectively. In contrast to biomass, modeled primary productivity was

maximal in summer, reaching values of 0.5-1 gC m-2d-1 in the northern half of the bay. This also agrees well with the field data of Harding et al. (1986), although Malone et al. (1988) reported maximal productivity values of 1-5 gC m-2 d-1 in the same location in summer.

There is a clear spatial pattern in the model results in figure 17. Biomass and primary productivity were low in the northern Bay near the Susquehanna River as a result of light limitation, in agreement with field data (e.g., Harding et al. 1986). Productivity and biomass were maximal at all seasons in the upper half of the Bay and decreased toward the ocean as a result of nutrient limitation. The model results also successfully reproduced a chlorophyll maximum in the middle of the Bay, in agreement with oceanographic observations (e.g., figure 6). Thus it is evident that the model successfully simulated at least some of the temporal and spatial aspects of observed algal biomass and productivity in the base-case scenario.

6.3 Modeling of Estuarine Scale Responses to Nutrient Reductions

The 3D model predicted decreased algal biomass in response to reductions in nutrient inputs. When both N and P were reduced to the limit of technology (LOT NP) described above, simulated phytoplankton biomass in the surface mixed layer declined by 5-40% relative to the base case throughout the Bay (figure 18). Reductions in biomass 30% were predicted to occur under LOT NP loading in the upper Bay in spring, summer, and fall, whereas more moderate reductions in biomass (5-30%) were predicted in the upper Bay in winter and in the lower Bay throughout the year.

Simulated nutrient load reductions for N or P alone were less effective in controlling algal biomass. In the northern Bay in zones 1-4 above the Potomac River, modeled responses to P reductions alone under the LOT P scenario were very similar to those of LOT NP in winter and spring (figure 18); however, the response to LOT P decreased in summer and approached half of that of LOT NP in fall in the upper Bay. Consistent with the strong effect of P reductions, N reductions in the LOT N scenario had little effect on simulated algal biomass in the upper Bay in winter and spring (generally <= 10%), but the response to LOT N increased in summer and approached that of LOT NP by fall.

The lower Bay responded quite differently from the upper Bay. In Virginia waters, zones 5-8, application of LOT N reductions always had the greatest effect on algal biomass in surface waters (10-30% reductions), equaling or exceeding the responses to LOT NP at all seasons. In contrast, LOT P

reductions had little effect (

For each season there was a distinct spatial separation of the effectiveness of the LOT P and LOT N strategies. The crossing of the LOT N and LOT P curves in figure 18 marks the boundary between significant responses to N or P reductions alone, and occurred within the restricted salinity range of 11 to 18 psu. Furthermore, the crossover point shifted down-bay in winter and spring and up-bay in summer and fall, suggesting that the effectiveness of LOT N and LOT P was related to runoff and the relative balance of fresh water and seawater in Chesapeake Bay. This observation further indicates the importance of seawater in the Bay's nutrient sources.

These modeled responses may be viewed as large-scale nutrient reduction bioassays. Using the classification scheme for bioassays shown in figure 9, the responses in the upper Bay correspond to exclusive or primary P limitation of biomass accumulation in winter and spring, which gradually changed into exclusive or primary N limitation from summer to fall. The simulated pattern of biomass reductions in the upper Bay shown in figure 18 is similar to that in experimental studies showing primary and exclusive P limitation of algal growth rates in spring and primary and exclusive N limitation in summer and fall in Maryland waters of the Bay (figures 10, 11, and 15). However, modeled estuarine-scale responses in winter exceeded those predicted by experimental measurements of growth rates, which indicated light limitation at this time of year, and modeled estuarine-scale responses did not show a brief period of P limitation in the fall following overturn (see figures 10 and 11).

Modeled responses to nutrient inputs can be similarly classified for the lower Bay. These responses correspond to exclusive N limitation throughout the year. In the lower Bay the model does not show winter light limitation or the brief period of P limitation of growth rates observed in the lower Bay in spring (Fisher et al. 1992a, Haas and Wetzel 1993; see also figure 11); however, this may be attributable to seasonal averaging of the model output. Although there are differences between the empirical and modeled data, the modeled estuarine-scale responses concur with the empirical data in the greater importance of N limitation in the higher-salinity waters near the ocean.

These model results support the temporal and spatial variations in algal growth rates observed in bioassays. The simulations suggest that, at the estuarine scale, algal biomass accumulation in the upper Bay is primarily P limited in winter and spring, changing to primary N limitation by fall. This

pattern is consistent with the observed distributions of DIN and PO4 and the great excess of DIN relative to PO4 that enters the upper Bay in inflowing fresh waters (Fisher et al. 1992a). The model results also predict that algal biomass accumulation in the lower Bay is exclusively N limited for the entire year, which is only partially consistent with bioassay results and observed distributions of DIN and PO4.

The spatial differences between the upper Bay and lower Bay may be caused by a net import of oceanic P. Both the 3D model and nutrient budgets for the Bay and its tributaries (Boynton et al. submitted) indicate significant contributions of oceanic P to Chesapeake Bay. Model results for the base-case scenario showed that there was a net import of 8.2 x 106 kg oceanic total P y-1, which is equivalent to 47% of the terrestrial load (Thomann 1993). Similarly, Boynton et al. (submitted) computed oceanic P input as followsoceanic P input = terrestrial input + direct atmospheric deposition - burial - fish harvest. Although the approach taken by Boynton et al. (submitted) was different, the computed oceanic P input (4.11 x 106 kg total P y-1) was similar to that of the 3D model and was equivalent to 37% of the estimated direct atmospheric and terrestrial P inputs. There is, however, considerable uncertainty regarding the form in which P enters the Bay from the ocean. In contrast, both the 3D model and the budgets of Boynton et al. (submitted) indicated a net export of total N, primarily as organic N, from the Bay to the ocean (31.6 x 106 kg total N y-1 per the 3D model and 45.9 x 106 kg total N y-1 per Boynton et al.). The concordance of these results using two methods indicates that oceanic P inflows to Chesapeake Bay are significant and are probably responsible for the differences in response to P reduction between the upper Bay and lower Bay. Furthermore, the net export of organic N shows that the Bay is efficiently processing terrestrial N inputs into organic material that is consumed internally and exported seaward.

The management implications of these simulations are clear. Reductions in P inputs appear to be most important in improving water quality conditions in the upper Bay in winter and spring, and will probably reduce the magnitude of the northern Bay s contribution to the spring bloom. In contrast, reductions in N inputs are required to improve water quality in summer and fall in the upper Bay and for most of the year in the lower Bay. Both the experimental and model results clearly support the justification for reductions in both N and P in fresh waters entering Chesapeake Bay to reduce the accumulation of organic matter that leads to anoxia.

6.4 Simulations of the Effects of N and P Reductions on Anoxia

The effects of nutrient reductions on the extent and duration of anoxia in bottom waters have also been explored with the 3D model at the estuarine scale. For the model simulations, anoxia was defined as dissolved oxygen (DO)

The 3D model was used to predict DO throughout the Bay under base-case conditions and average runoff (figure 19). There was a consistent undersaturation of simulated DO in the deep trench area of the upper Bay (150-250 km from the mouth of the bay) irrespective of season. This area corresponds to the Pleistocene channel of the Susquehanna River that was cut during the previous glaciation at a low sea level stand, and that has filled more slowly with sediment than the subsequent rise in sea level (Meade 1968). The model predicted a rapid drop in DO during the spring and summer in this area of the Bay, and anoxia was predicted in summer for a 40 km stretch of bottom waters located ~220 to ~260 km from the mouth of the bay, in the vicinity of the Chesapeake Bay Bridge at Annapolis. This stretch corresponds to the region in which field and modeled algal biomass and primary productivity were greatest (e.g., figure 17). The duration and extent of anoxia in summer was computed as 300 x 109 m3 d under base-case conditions.

These predicted values of DO agree qualitatively with the Baywide observations of Officer et al. (1984) and Harding et al. (1992). Both the timing and location of the modeled DO correspond to those observed in Bay monitoring programs. However, the spatial extent predicted by the 3D model is less than that observed in field observations.

One of the important questions concerning anoxia is its relationship to nutrient inputs. How much reduction in nutrient inputs is necessary to decrease volume-days of anoxia? To address this question, the 3D model was used to simulate DO in the Bay under the scenarios listed in table 6. In addition to the LOT NP, LOT N, and LOT P scenarios discussed above, other scenarios of nutrient input reductions were used to explore the relative importance of N and P in controlling the extent and duration of anoxia. The model results from each scenario, expressed as volume-days, were computed as a percent reduction in base-case conditions under average hydrology.

None of the currently achievable strategies for nutrient reductions in the Bay s watershed resulted in large reductions in anoxia in the model simulations (figure 20). Application of the LOT NP and LOT N scenarios resulted in ~30% reduction in volume-days, whereas there were 15-20% decreases in volume-days under LOT P and the strategy for 40% reductions in the controllable loads (the current strategy under the tristate agreement). These

results are consistent with the those presented above for decreases in algal biomass simulated with the 3D model (figure 18) reductions in P loading decreased biomass in the upper Bay during winter and spring, but N controlled biomass accumulation in summer and fall in the upper Bay and throughout the year in the lower Bay. These results emphasize the probable importance of estuarine-scale sedimentation and circulation on the development of anoxia (figure 7), and suggest that the current 40% reduction strategies will have only a small effect (~20 %) on the duration and extent of anoxia.

Only large reductions in simulated nutrient inputs had a substantial effect on the duration and extent of anoxia (figure 20). For example, 50% reductions in the current total N and total P inputs reduced anoxic volume-days by ~60%, and anoxia was completely eliminated if N and P loadings were decreased by 90% in the model. This last scenario is an approximation of undisturbed conditions prior to European settlement (e.g., Nixon and Pilson 1983), and it is unlikely to be achieveable.

These results provide evidence that Chesapeake Bay is an estuary predisposed to the development of anoxia. The overdeepened channel in the middle of the Bay is a natural trap for organic matter, and the estuarine circulation provides a limited supply of oxygen that is readily exceeded by respiratory demands during the consumption of organic matter made available by vertical and horizontal processes.

In the model simulations, a 90% reduction in P alone had a small effect on anoxia (figure 20). This strategy was among the weaker ones in terms of controlling anoxia, probably because of the supply of P from inflowing seawater and because the effect of LOT P was shown to be a displacement of the chlorophyll maximum from the P-limited upper Bay toward higher salinity N-limited waters in the lower Bay. Regardless of the position of the chlorophyll maximum, the countercurrent circulation will carry sedimenting organic matter produced in surface waters back toward the overdeepened channel as particulate or dissolved material, where it will still contribute to anoxia(figure 7).

These results strongly support the need to control both N and P inputs to Chesapeake Bay from the Bay s watershed. Although it is unlikely that anoxia will be eliminated in bottom waters, it appears to be possible to achieve reductions of ~30% in anoxic volume-days and algal biomass by application of LOT NP techniques in the watershed. Little improvement and some

deterioration in Virginia waters can be expected from using a LOT P strategy. The importance of N appears to result from the supply of P from the ocean, as shown above.

7. Conclusion

This paper provides a comprehensive overview of the linkages among nutrient limitation, algal growth rates, biomass accumulation, and anoxia in Chesapeake Bay. A conceptual framework for nutrient limitation illustrates the effects of scaling, and is used as a basis for examing the linkages on two scalesthe local and estuarine scales. A review of the freshwater and marine literature shows that, although there is a strong experimental and practical basis for using P management for lake restoration in the temperate zone, the evidence for N limitation in marine systems is less substantial, primarily because of the larger scales of marine systems and the greater inherent difficulties of experimental manipulation. The existing experimental evidence supports N limitation of temperate marine systems and P limitation of shallow tropical systems with calcareous sediments. Temperate estuaries, with their seasonally varying mixtures of fresh water and seawater, are shown to have seasonal variations in N and P limitation.

On the basis of experimental studies of nutrient limitation in Chesapeake Bay, there is strong evidence for a seasonal progression in light, P, and N limitation of algal growth rates through winter, spring, and summer/fall at the local scale. It is also evident that nutrient concentrations and ratios are imperfect indicators of nutrient limitation. Modeling studies have successfully simulated many of the temporal and spatial aspects of observed algal biomass and productivity, and have provided corroborating evidence for the dual importance of N and P in the control of algal biomass and anoxia at the estuarine scale. Both experimental and modeling studies show the greater importance of P in controlling growth rates and accumulation of biomass in spring in the upper Bay, but they emphasize the necessity of N reductions to achieve these objectives in summer/fall in the upper Bay and throughout most of the year in the lower Bay. Because of the countercurrent circulation in estuaries, oceanic P inputs, and spatial variations in the limiting nutrient, reductions in P inputs alone are likely to have little effect on the accumulation of algal biomass or the extent and duration of anoxia. Model results also suggest that anoxia is likely to persist under current nutrient control strategies and that only large reductions in N and P inputs approaching those

of undisturbed watersheds will significantly reduce the annual anoxic volume in Chesapeake Bay.

This paper also identifies two research recommendations related to the scale of nutrient limitation in estuaries. The relative importance of local sedimentation and horizontal advective delivery of organic matter by way of the estuarine circulation to bottom waters appears to be unknown in Chesapeake Bay. Information on the relative importance of these processes is relevant to the ability of growth rate bioassays of surface waters (the local scale) to indicate the potential contribution of local biomass to the development of anoxia. If this information were available, it might identify critical regions of the Bay (geographic or hydrographic) in which local sedimentation is dominant and which could be used to monitor the sucess of nutrient abatement programs in the Bay s watershed. This question is not easily addressed by experimental measurements, but is amenable to modeling approaches.

A second research recommendation concerns the investigation of the spatial variation in resource limitation along the entire length of the Chesapeake Bay mainstem.There is only one year (1992) with sufficient temporal and spatial sampling to examine an annual cycle of spatial variation along the entire length of the Bay (figure 11). There are likely to be large interannual variations in the spatial distribution of resource limitation owing to, for example, the effects of river hydrology (figure 10). In addition to providing a better understanding of resource limitation at the estuarine scale, Baywide data would also be an excellent monitoring tool with which to examine the effectiveness of watershed management actions.

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Atmospheric Deposition of Nitrogen and Contaminants to Chesapeake Bay and Its Watershed

Richard A. Valigura, Joseph Scudlark, Joel E. Baker, and Laura L. McConnell

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1. Introduction

Despite continuing attempts to control nutrient loads at the source, overenrichment of U.S. estuarine and coastal marine environments remains a serious problem that affects recreation, the harvesting of living marine resources, and human health. These problems are being exacerbated by the concurrent and chronic nonpoint loadings of chemicals that have biogenic and toxic effects.

Over the last 30 years, it has become clear that concentrations of nitrogen and chemical contaminants in the water are related not only to point source inputs into the riverine and estuarine systems, but also to atmospheric inputs, both direct and indirect. Numerous studies have explored the idea that atmospheric deposition may contribute a significant proportion of phytoplankton nitrogen demands in coastal areas (Paerl 1985, 1988, Paerl et al. 1990). Fogel and Paerl (1991), for instance, have estimated that 20-50% of annual new nitrogen demands for Pamlico-Albemarle Sound may be supplied by direct atmospheric deposition to the water surface (wet and dry). Furthermore, there have been two recent, and opposing, papers published on the effects of wet deposited nitrogen on phytoplankton off Bermuda (Owens et al. 1992, Michaels et al. 1993). Several recent studies have attempted to quantify the atmospheric nitrogen loads delivered to Chesapeake Bay, with the first such effort conducted by the Environmental Defense Fund (EDF) arriving at a rough estimate of one-third of the total inorganic nitrogen entering the Bay (Fisher et al. 1988).

However, all studies to date reflect the difficulty of estimating with accuracy the exact amount of material entering an estuary from the atmospheric pathway. The frequency and magnitude of contaminant loadings events are thought to be increasing, but there is not yet a strong enough basis for recommending specific actions to prevent such events. Accordingly, if total loadings to Chesapeake Bay are to be substantially reduced as mandated by the Chesapeake Bay Program it is essential to have a full understanding of the Bay, and that, in turn, necessitates having a full understanding of chemical

cycling within the entire Bay ecosystem.

The biogeochemical cycling of nitrogen and contaminants on local, regional, and global scales is a complex system of emissions, transformations, dispersion, and deposition. This system is most complex in coastal environments, such as Chesapeake Bay, where landscape processes affect coastal processes and vice versa. Figure 1 is a simplified schematic that shows an idealized picture of the Chesapeake Bay system divided into four basic compartments/reservoirs, and the transfers among them. It has proven convenient to adopt such a systematic view of the environment. This view is the basis for the current mass balance paradigm that attempts to quantify the transfers (loadings) between designated system components. To date, most emphasis has been placed on quantifying and identifying direct, well defined emissions to each compartment (i.e., emissions from smokestacks, outfalls). However, the terrestrial watershed and the riverine and estuarine processes affect the transport of these emissions to the Bay, both directly and indirectly. These effects are not currently quantified to any significant degree and represent a major research need.

Atmospheric deposition includes wet deposition and dry deposition (see sidebar). In each case, it also is necessary to consider whether the deposition is deposition to the water surface (i.e., direct deposition) or deposition to the watershed, with subsequent transport to the receiving stream (i.e., indirect deposition). Determining the magnitude of deposition is necessary, but not always sufficient, for addressing management issues. To deal efficiently with such issues requires an understanding of both the sources of atmospheric contaminants (e.g., long-range versus short-range transport, type of emission source) and the relative magnitude of the atmospheric depositional loadings compared to that of all other sources of contaminants to surface waters.

The goal of this paper is to summarize the technical issues associated with the emission, transformation, dispersion, and deposition of nitrogen and nitrogen compounds, persistent organic pollutants, and trace elements; evaluate the current understanding of the magnitude and relative importance of atmospheric deposition to Chesapeake Bay and its watershed; and identify the key steps that should be considered as a means of reducing the uncertainty in developing estimates of atmospheric depositional loading.

1.1 Glossary of Terms and Abbreviations

Deposition, dry:

The unidirectional flux of chimcals from the atmosphere to an underlying suface (other than during precipitation events). The rate of deposition is regulated by chemical, physical, and biological phenomena. Depending on the chemical involved, dry deposition can be less than, equal to, or greater than wet deposition.

Deposition, wet:

The flux of materials from the atmosphere to the earth's surface during precipitation and fog events.

Emission:

The flux of material into a compartment (figure 1). Emissions into the atmosphere include emissions from point sources (e.g., smokestacks), emissions from mobile sources (e.g., motor vehicles), and fugitive emissions (e.g., from volatilization and resuspension).

Flux:

The rate of transport of a material across an interface. For example, the flux of nitrogen moving from soils to groundwater may be expressed as kilograms of nitrogen per hectare per year (Kg N ha-1 yr-1).

Loading:

The total mass of material entering an environmental reservoir (e.g., the atmosphere, a water body) in a given time. Loadings are estimated by extrapolating measured site- and time-specific fluxes over larger spatial and temporal scales. For example, the loading of benzo[a]pyrene to Chesapeake Bay may be expressed as kilograms per year (Kg BAP yr-1).

Resuspension:

The removal of deposited particles from a surface (fluid or solid) by fluid flow above the surface. A particle deposited to a surface is subjected to adhesion forces and fluid lift and drag forces. The balance among these forces determines whether or not the particle is resuspended in the atmosphere.

Transformation:

The chemical alteration of materials. Transformations include the complete conversion of materials to primary components, as well as the

partial conversion to other, possibly more stable, intermediates.

Volatilization:

Reemission of previously deposited gaseous species adsorbed/absorbed to a surface into the atmosphere owing to many, primarily chemical, factors. There factors include chemical reaction, vapor pressure, gas-particle partitioning, temperature, and wind speed.

2. Nitrogen Compounds

Most nitrogen compounds (excluding N2 and N2O) fall into two categoriesreactive nitrogen and reduced (ammonia) nitrogen. Although technically a reactive nitrogen species, organic nitrogen compounds are often discussed as a separate category, owing to their complexity.

2.1 Reactive Nitrogen

Total reactive nitrogen is termed NOy because it consists primarily of oxides of nitrogen. NOy is defined as follows

NO = NOx + HONO + HNO3 + HO2NO2 + 2[N2O5] + PAN + RONOx + pNO3-,

where NOx represents the sum of the concentrations of nitrogen oxide (NO) and nitrogen dioxide (NO2) (Fehsenfeld et al. 1987). Of the NOy components, nitric acid (HNO3) and particulate nitrate (p-NO3-) are thought to be the primary compounds of nitrogen deposition (Huebert et al. 1988, Meyers et al. 1989); NO2 deposition also may be significant in a near-urban environment when the NO2 concentration is high, and its spatial and temporal extent is an important question being addressed. Like most of the NOy components, HNO3 and p-NO3 are secondary products derived from the NOx compounds (figure 2). Of the remaining elements of NOy (i.e., nitrous acid [HONO], peroxynitric acid [HO2NO2], dinitrogen pentoxide [2(N2O2)], peroxyacetyl nitrate [PAN], and organic nitrogen [RONOx]), only RONOx is suspected of making significant contributions to deposition estimates (Smullen et al. 1982). The majority of reactive nitrogen released into the atmosphere by either anthropogenic or natural sources is in the form of NOx (90-95% is NO). A global NOx budget by source is presented in table 1 in the form of terragrams (1 Tg = 10 X 12 g) of nitrogen per year.

Current global emission estimates for nitrogen oxides are listed in table 1.

Anthropogenic emissions of NOx constitute over 50% of the global budget. Of this proportion, the majority is attributed to high temperature combustion (of coal, oil, gasoline, etc.) regardless of whether or not the fuel has a nitrogen content (Clarke 1992, NAPAP Acid Precipitation Task Force 1993). It is important to note that the degree of uncertainty in many of these estimates is high, typically varying from a factor of two to an order of magnitude. This high uncertainty is largely attributable to the lack of a standardized or even widely accepted method for measuring or monitoring the average rates of emission of trace chemical species between the atmosphere and the surface. The alternative is to use a limited amount of information on localized exchange and extrapolate averages of the values that are truly required. This limitation applies especially to the case of natural emissions, but also extends to the cases of industrial and automotive sources.

Computer modeling is considered the most viable method for extrapolating site-specific, local measurements of emissions to large areas, and for then assessing the impact of these emissions on distant areas downwind (Pielke 1984, Fisher 1992, Koch 1993). The majority of atmospheric modeling studies to date have incorporated emissions estimates derived during the acid rain debate of the 1980s (U.S. Environmental Protection Agency 1986). However, these estimates have recently been refined. In 1991 the U.S. Environmental Protection Agency (EPA) (U.S. Environmental Protection Agency 1991a, NAPAP Acid Precipitation Task Force 1993) released an updated NOx emissions data set (see table 2). These estimates are currently considered to be preliminary, but they differ substantially from the 1985 estimates that have been the basis for all modeling work done using emission data bases in the Chesapeake Bay region (Pechan 1991, 1992, Dennis 1994). Using the 1991 data base, EPA scientists are currently reevaluating assessments of probable reductions in deposition to the Chesapeake Bay watershed resulting from the Clean Air Act Amendments of 1990 (CAAA). The 1990 emissions estimates, measured in gigagrams N yr-1 (1 gigagram [Gg] = 10 x 9 g), that are currently being used for these studies are presented in table 3 by different economic sector source within and around the Chesapeake Bay watershed (Dennis 1994). Owing to implementation of the CAAA, it is expected that emissions of NOx in the year 2000 will be 10% lower than for the base year of 1980. However, because the CAAA contain no legislated cap for NOx emissions, emissions are expected to increase again in the next century (NAPAP Acid Precipitation Task Force 1993). The processes and/or interactions among emissions, concentration, and deposition are very nonlinear; therefore, it cannot be said that reducing emissions by a certain percentage will reduce

deposition by the same amount. The underlying science is currently one of the primary areas of research in atmospheric sciences.

Although reactive nitrogen released to the atmosphere as NO and NO2 is ultimately oxidized to HNO3 and p-NO3- before deposition to vegetation and other components of the earth s surface (see figure 2), the time constant for this conversion varies from several hours to days depending upon location, season (light intensity and temperature), humidity, and level of photochemical activity (Logan 1983). Given the wide range in the rates of wet and dry deposition of the species that constitute NOy (i.e., NO, PAN

This issue has special relevance to Chesapeake Bay, as follows. In the area centered on the Baltimore-Washington corridor, the NOy emitted is predominantly in the form of NO and NO2. In urban and near-urban areas, the ambient NO2 concentrations can reach much higher levels than in more rural environments (M-szÊros 1992). The deposition rate of NO2 is much lower than that of HNO3 (that of NO is virtually zero), and because both NO and NO2 are largely immune to removal by wet deposition, NOx emissions may well be advected from, not deposited to, the Bay watershed. However, even though the dry deposition rate of NO2 is small, it is not negligible, and high NO2 concentrations may promote significant amounts of deposition.

There is also an annual trend in species distributions and concentrations. Emissions of NOx are highest in the winter, but during the summer, when photochemical conversion and atmospheric instability are at their peak, deposition of Baltimore s NOy emissions to the Bay may be at a maximum. Therefore, it is important to begin concurrent monitoring of the concentration and deposition for the suite of NOy species to ensure accurate deposition estimates.

2.2 Ammonia Nitrogen

On a global basis, microbial decomposition of organic nitrogen compounds in soils constitutes the major source of NH3 deposited to the troposphere (Levine et al. 1980, Georgii and Muller 1974, Georgii and Lenhard 1978). Two sets of recent estimates of the global NH3 budget are presented in table 4 (Schlesinger and Hartley 1992, Dentener and Crutzen 1994). The large differences between the two sets illustrate the uncertainty involved in global estimations.

Of prime importance to Chesapeake Bay and the surrounding watershed is the release of NH3 from commercial and organic fertilizers (including liquid

anhydrous NH3 applied to crops). Factors that influence the release rate of NH3 include soil type and moisture content, pH, and temperature, as well as the size of the fertilizer grains, the amount of fertilizer used, the depth to which the fertilizer is incorporated, and irrigation frequency (Gravenhorst and Bottger 1980). Volatilization from animal wastes also can be an important source of NH3 (Healy et al. 1970, Gravenhorst and Bottger 1980, Lenhard and Gravenhorst 1980), particularly in areas, such as the Delmarva Peninsula, where the poultry industry constitutes a major agricultural activity. The importance of fossil fuel combustion in ammonia s budget remains uncertain (Eriksson 1952, Stedman and Shetter 1983). Release of NH3 from urban areas may be important, however, depending upon the specific mixture of industrial and commercial activities unique to each such area.

On a seasonal basis, NH3 concentrations are generally highest in spring and summer, when increased fertilizer usage combines with warmer temperatures to promote greater microbial activity in and faster volatilization rates from fertilizers, soils, and animal wastes. Whether NH3 concentrations peak in spring or summer at a given location probably depends upon the relative strengths of local sources. In agricultural areas, springtime maxima likely result from rapid volatilization from fertilizer applied at the beginning of the growing season (Levine et al. 1980, Hoell et al. 1980, Cadle et al. 1982). In more remote areas, NH3 concentrations most likely peak in the summer, when release from natural soils dominates the local budget (Georgii and Lenhard 1978). Levels of ammonia are generally at a minimum in winter, when biological activity in the soil and rates of volatilization are low (Georgii and Muller 1974, Georgii and Lenhard 1978, Tanner 1982). Similarly, concentrations tend to be lower at night, when NH3 release slows owing to lower temperatures and diminished microbial activity. These physiochemical considerations are countered by boundary layer dynamics, however. A shallow inversion during the night may inhibit ammonia deposition and disperse gas-phase NH3 into a smaller volume; both effects have a tendency to raise ambient NH3 concentrations at night.

Current understanding of sources and sinks for ammonia is limited by the lack of reliable techniques for determining NH3 in real time at low concentrations (

2.3 Organic Nitrogen

To date, studies of atmospheric nitrogen deposition have almost exclusively addressed dissolved inorganic nitrogen, deposited in rain and snow. Because

of the paucity of reliable measurements and the variability in analytical techniques and results, only limited work has been done on organic nitrogen (Gorzelska and Galloway 1990, Gorzelska et al. 1992, Mopper and Zika 1987). The few available data suggest that the contribution of the unresolved organic fraction may significantly augment the atmospheric deposition of nitrogen to coastal waters. Given a value for the average dissolved organic nitrogen (DON) concentration in precipitation that might be depositing to Chesapeake Bay of approximately 7 micromol l-1 (an approximate value on which a number of the cited studies converge), the total atmospheric nitrogen loading would increase by 10-15% over current estimates. Data summarized by Smullen et al. (1982) indicate that atmospheric DON deposition to Chesapeake Bay (<= 6 kg ha-1 y-1) could increase the total annual nitrogen flux by as much as 43%. Regardless of the apparent discrepancy, either estimate would represent a significant contribution to the level of overall atmospheric nitrogen loading to the Chesapeake. Although a determination of sources and sinks of organic nitrogen compounds as well as of ammonia is ultimately needed, there is currently little information available regarding the proper measurement of organic nitrogen compounds.

A key consideration in the debate about organic nitrogen is the extent of the association between sources and sinks. In some instances, measured DON is related to emissions or sources that are very near the measurement site, and hence the deposition measurements do not constitute an indication of a flux of DON into the Chesapeake Bay watershed as a whole. Rather, they might be viewed as evidence of a redistribution occurring within the watershed ecosystem. The extent and importance of this possible redistribution are presently unknown, and the topic can best be viewed as contentious.

2.4 Loading Estimates

The role of atmospheric transport in providing an important path for nitrogen to estuarine areas was publicized in the EDF report (Fisher et al., 1988). Based on one year of measurements (1984), and assuming relationships between wet and dry deposition that are likely to be conservative, the authors estimated that one-third of the inorganic nitrogen entering Chesapeake Bay comes from the atmosphere. There have been several subsequent efforts to quantify the atmospheric nitrogen loadings to the Bay. The approach taken in these studies can be divided into two componentsestimating wet and dry deposition and estimating watershed retention. However, the assumptions used in these studies overshadow the results; the error associated with these estimates is typically quoted as being a factor of two or sometimes as much as

a factor of about three (Fisher and Oppenheimer 1991, Hinga et al. 1991, Tyler 1988).

Wet and Dry Deposition

The Bay studies cited above incorporate wet-deposition data from the National Atmospheric Deposition Network (NADP) to estimate deposition for one particular year, 1984, with average rainfall. The NADP network, initiated in 1978, consists of some 193 sites funded on a site- to-site basis by a variety of organizations. These sites have identical siting and sampling criteria, and all data are analyzed in the same laboratory and using the same methodology. Precipitation samples are collected for one week with wet-only samplers and then sent to the Illinois State Water Survey for analysis. The standardization of sampling and analytical protocol within NADP enables site comparisons to be made. Measurements of the wet deposition of NO3 and NH4 from the 12 NADP sites in and around the Chesapeake Bay watershed for the years 1984-91 are presented in tables 5 and 6. As shown, there are considerable interannual differences at a given site as well as intersite differences.

The primary assumption made by the Bay loading studies is that dry deposition is equal to wet deposition. This assumption is necessary because there is no independent measurement basis for estimating areal dry deposition rates. This same lack of data also means that there is no existing evidence that this estimate is grossly misleading. It would seem obvious, considering the vastly dissimilar atmospheric and surface mechanisms that cause dry and wet deposition, that equality between them would be an extremely unlikely and quite fortuitous finding, in practice.

The primary network estimating dry deposition is the National Oceanic and Atmospheric Administration s Dry Deposition Inferential Measurement (DDIM) network. The DDIM network, which currently has twelve dry deposition sites (two in the Chesapeake Bay watershed), estimates dry deposition of p-NO3, and HNO3 by heated inlet filterpacks. Most DDIM sites are collocated with precipitation chemistry sites, thereby making it possible to estimate total NO3 deposition. Table 7 presents data from sites that measure both wet and dry NO3 deposition at the same location.

Direct Loadings to the Bay

It is not currently known if the over-land measurements are representative of over-water deposition, but it is suspected that this is not the case. Estimates of wet deposition to the Chesapeake Bay surface range from 3.45 to 4.2 Gg NO3-

N yr-1 (Fisher and Oppenheimer 1991, Hinga et al. 1991, Tyler 1988). Although the air/surface exchange of nitrogen has been estimated for most nitrogen species over open ocean (Galloway 1985, Duce et al. 1991), these rates may not apply to coastal situations in that coastal areas involve different meteorological processes (National Research Council 1992). Through the use of instrumented Chesapeake Bay Observing System (CBOS) buoys, owned by the University of Maryland, estimates of nitrogen (HNO3, NO2, NH4) dry deposition rates to the Bay surface have been developed (Valigura et al. 1993). These estimates corroborate those given by other investigators to some extent, but still cover a wide range of values, from 745 Mg y-1 to 2.24 Gg y-1. From this data set, calculations were performed to determine the effect of atmospheric dry deposition on phytoplankton dynamics. This analysis demonstrated that dry deposited nitrogen may provide 10% of the annual new nitrogen demands in Chesapeake Bay, and that individual events could supply up to 75% of the new demands for periods of several days (Malone 1992, Owens et al. 1992).

Indirect Loadings

The greatest uncertainty in the quantification of loadings to coastal areas such as Chesapeake Bay is how much is transferred through the terrestrial watershed to the surface waters, and how much is subsequently transported downstream to the Bay. Nitrogen activity within a given watershed depends on the amount of soil nitrogen, historical acidic deposition, physical characteristics of the soil, site rainfall and temperature characteristics, the elevation and slope of the land, and the type and age of the vegetative cover (see figure 3). These characteristics vary at all scales, making it difficult to determine the general fate of atmospherically deposited nitrogen over any area of significant size. However, using these criteria, a classification scheme for forested sites has been developed to evaluate a site s potential to retain/leach nitrogen (Melillo et al. 1989, Johnson and Lindberg 1992). Sites in the Bay watershed generally fall into the leaching classifications of zero to low (Hunsaker et al. 1994).

A central difficulty in all discussions of watershed retention relates to the use of average values in assessments. Watershed retention assumptions used in the Chesapeake Bay studies (see above) are presented in table 8. These assumptions vary over several orders of magnitude, primarily because of the lack of adequate evaluation data. Assembling an adequate understanding of long-term behavior when the processes involved are fundamentally episodic is one of the major challenges, and represents an area in which contemporary

models appear sorely deficient. This problem necessitates the establishment of integrated monitoring sites. Integrated monitoring recognizes that monitoring networks should include a subset of sites where many activities are conducted in concert, addressing all relevant media and across the issues of the day (Hicks and Brydges 1994). These sites would facilitate the investigation of the amount of atmospherically deposited nitrogen and contaminants that migrate through watershed ecosystems. A key consideration in such studies is the concurrent measurement of the chemistry, intensity and duration of precipitation and streamflow events. It is apparent from measurements that the majority of the atmospheric wet deposition occurs during a few episodes (Dana and Slinn 1988, Fowler and Cape 1984), such that the wet deposited nitrogen (as well as previously dry deposited nitrogen) is deposited directly to or can flow quickly into the surface waters without intermediate reduction in concentration.

Comparisons

Chesapeake Bay is not the only East Coast estuary impacted by nitrogen deposition. Studies performed on several other major East Coast estuaries, from Pamlico-Albemarle Sound to the Gulf of Maine, have provided atmospheric nitrogen loading estimates that range between 18% and 39% of the total nitrogen load. However, there are many areas along both the East Coast and the Gulf of Mexico that remain to be investigated. The uncertainties of the studies to date make it imperative that a better understanding be obtained of the processes that transport and deposit nitrogen to estuaries and coastal zones. A summary of nitrogen loading estimates to many coastal areas around the country is presented in table 9. It has also been suggested that the transport of nitrogen to the open oceans may have an impact on biological activity in remote regions. The atmospheric movement of nutrients has both global and local implications that necessitate regional coordination of local issues.

3. Persistent Organic Pollutants

Persistent organic pollutants are released into the environment in increasing amounts as a result of anthropogenic activity. The often toxic nature of these compounds is of great concern. If released to the atmosphere, many of the more long-lived compounds may be transported through atmospheric processes to ecologically sensitive areas. Some general classifications of these

contaminants and their sources are listed in table 10.

The transport, fate, atmospheric residence time, and removal processes for organic compounds are largely determined by the distribution of the semi-volatile organic chemical (SOC) between the gas and particle (G/P) phases (Bidleman 1988, Junge 1977, Ligocki et al. 1985a, 1985b, Eisenreich et al. 1981, Pankow 1987, Duinker and Bouchertall 1989, Ligocki and Pankow 1989, Foreman and Bidleman 1990). In general, the G/P distributions are a function of the vapor pressure of the organic compound, the ambient temperature, and the concentration, size, and composition of atmospheric particulate matter. Junge (1977) described G/P distributions in the atmosphere using a Langmuir isotherm as

phi = [cp/(cp + cg)] = c(phi)/(p(SUP o) + c(phi)),

where phi = fraction of compound in particle phase
cp = particle-phase concentration of SOC in atmosphere (ng/m3)
cg = gas-phase concentration of SOC in atmosphere (ng/m3)
p(sup o) = vapor pressure of SOC (torr)
c = a constant (equal to 0.13)
c = concentration of total suspended matter in atmosphere expressed as surface area (cm2/cm3)

Junge (1977) and others have used this equation to describe the general distribution of SOCs between the G/P phases in the atmosphere as a function of increasing p(sup o) by plotting (cp/cg) = log (1-phi/phi) versus log cp(sup o), where the intercept is log (1/cT). It may be expected that c is a function of compound class and therefore constant within that class and representative of the difference of the enthalpy of desorption of the compound from particulate matter and vaporization of the pure compound (Pankow 1987).

Seasonal variations in atmospheric SOC concentrations and G/P distributions have been actively investigated (Manchester-Neesvig and Andren 1989, Hermansen and Hites 1989, Hoff et al. 1992a) and inevitably reflect source emissions and the effect of temperature on vapor pressure. Hoff et al. (1992a) determined atmospheric concentrations of polychlorinated biphenyl (PCB) congeners and many organochlorine pesticides in 143 samples collected in 1988- 89 in Egbert, Ontario. This high-resolution data set provides the definitive evidence of the seasonal (i.e., temperature) control on atmospheric SOC concentrations. Hoff et al. (1992b) developed atmospheric source functions to describe the seasonal behavior of SOCs. Not surprisingly, SOC concentrations were closely correlated to temperature and to p(sup o)L. The seasonal source functions have been combined with temperature-dependent G/P distributions calculated using the Junge-Pankow model to estimate annual wet and dry loadings of numerous chemicals in the Great Lakes region (Eisenreich and Strachan 1992).

ging processes are important removal pathways for organic pollutants, photochemical transformations also may be extremely important for some compound classes. Organic pollutants may undergo a photolytic transformation in the atmosphere, on soil and leaf surfaces, and in the aqueous phase. The chemical structure of a contaminant determines its

susceptibility to this transformation process. The chemical may undergo either direct or indirect photochemical reactions in the gas phase, while attached to airborne particles, or while within a cloud or fog droplet (Klopffer 1992). Gas-phase reaction rates are difficult to measure, but hydroxyl radicals are probably the most important oxidant species for phototransformation of organic compounds in the atmosphere (Plimmer and Johnson 1991).

Relatively few studies have been carried out on the atmospheric phototransformation of pesticides. A laboratory study using a Teflon environmental chamber determined rate constants for organophosphorus insecticides and three radical species, OH, NO3, and O3 (Winer and Atkinson 1990). The fastest transformation rates were found for OH, followed by NO3 and O3. Polyaromatic hydrocarbons (PAHs) can react in the atmosphere with ozone, nitrogen oxides, and sulfur dioxide to undergo photooxidation (U.S. Department of Health and Human Services 1990a). Half-lives are estimated to range from 7 days for benzo(a)pyrene to 30 days for phenanthrene. PCBs also may undergo vapor-phase reactions with hydroxyl radicals. Half-lives under laboratory conditions were 3-6 days for monochlorobiphenyl congeners and 40-80 days for pentachlorobiphenyl congeners (Atkinson 1987). Table 11 presents a summary of available data on the half-lives of some organic pollutants attributable to gas-phase reactions with hydroxyl radicals.

Dry depositional fluxes are typically estimated using size-specific (i.e., crustal versus noncrustal) aerosol particle size distributions and dry deposition velocities (Wu et al. 1992). These estimates are highly uncertain and are generally taken as order of magnitude estimates. In general, the dry depositional loadings of particle-associated organic contaminants are substantially larger than wet deposition for those chemicals with vapor pressures less than approximately 17 Pa. Compounds that are extremely volatile (e.g., fluorene and many PCB congeners) rapidly dissolve into falling precipitation droplets, thereby resulting in an large wet flux relative to the dry flux. However, the dry depositional fluxes of organic contaminants are highly uncertain as very little is known about their particle size distributions in the atmosphere (Leister et al. 1994). Many of the less-volatile particle-associated compounds are likely on very small (i.e., less that 1 micron) particles with lower deposition velocities. In addition, little is known about changes in the size distributions of insoluble particulate matter as air masses travel over water.

3.1 Pesticides

Chlorinated hydrocarbon pesticides such as DDT, aldrin/dieldrin, hexachlorocyclohexane, chlordane/heptachlor, and toxaphene were the first pesticides to be widely used in the United States. By the late 1970s, however, evidence that these compounds were accumulating in the tissues of animals and having extremely toxic effects essentially ended their use in the United States and many other developed countries. Nevertheless, residues of these compounds continue to be observed in the air, rivers, oceans, and biota of even the most remote areas of the globe (Kucklick et al. 1993, Bidleman et al. 1994, Patton et al. 1991, Patton et al. 1989, Hinckley et al. 1991, Bidleman et al. 1989). Researchers have shown that atmospheric transport processes enable these chemicals to be very widely dispersed in the environment (Bidleman et al. 1989, McConnell et al. 1993).

The current generation of pesticides has been designed to be much less persistent, but

massive amounts of these chemicals are being used in close proximity to sensitive areas such as Chesapeake Bay, and they are cause for serious environmental concern. The need to keep pesticide losses from agricultural fields at a minimum is important not only to reduce costs for farmers but also to protect the important natural resources that Chesapeake Bay provides for the surrounding communities and the nation.

The current global usage of pesticides has recently been estimated at 2 Tg y-1 of active ingredients. The United States accounts for approximately one-third of this usage. Herbicides (53%) are the most widely used type of pesticide, followed by insecticides (29%) and fungicides (11%) (Aspelin et al. 1992). Table 12 summarizes the estimated annual usage of major pesticides in the United States as a whole, in the mid-Atlantic region, and in the Chesapeake Bay estuarine drainage area (Aspelin et al. 1992, Pait et al. 1992).

Pesticide loss to the atmosphere is regulated by the physical and chemical properties of the soil, application method, meteorology, soil moisture conditions, the presence or absence of a plant canopy, and the properties and formulation of the pesticide. Several attempts have been made to predict the behavior of pesticides in soil using computer simulation models. One such model is the Leaching Estimation and Chemistry Model (LEACHM) developed by Wagenet and Rao (1990). This model attempts to describe in detail the processes of evapotranspiration, water flow, pesticide movement in soil, application, degradation, volatilization, leaf and root growth, temperature, and pesticide uptake by plants. Each process is described by a time-dependent equation. This type of model is sensitive to very small changes in environmental conditions. However, owing to the complexity of the model, it requires advanced computing facilities to operate. Some other models require less information and only produce qualitative information. Another, less-demanding model is the Behavior Assessment Model for Trace Organics in Soil, developed by Jury et al. (1983). It attempts to describe the effects of application method, soil properties, degradation, volatilization, and sorption of the pesticide to the soil.

One of the most critical processes to measure is volatilization flux. A comparison of different approaches to measuring the volatilization flux is given by Majewski et al. (1990). The authors concluded, however, that there is no certainty that the results obtained by using these methods are accurate and that better methods for flux measurements are needed. A review of actual field experiments to measure the volatilization flux is given in Taylor (1994). Although it may be difficult to directly measure the volatilization flux, results from laboratory and field experiments and computer models have demonstrated that pesticide volatilization from a plant or other surface depends primarily on the vapor pressure of the compound and atmospheric turbulence. Increasing vapor pressure and turbulence leads to increased volatilization.

Pesticide movement in soil is affected by many factors, including soil moisture, soil organic carbon content, soil temperature, depth of incorporation, the air/water exchange constant (K (sub H)) of the pesticide, and the organic carbon exchange coefficient (K(sub oc)) of the pesticide. Table 13 gives the effect of each factor on volatilization. Specific laboratory studies of the effects of these factors and others on volatilization are available in the literature (Spencer and Cliath 1970, 1972, 1974, Spencer et al. 1973, Walker et al. 1992, Barriuso and Calvet 1992). Thus a situation in which a pesticide with a high K(sub H) value and a low K(sub oc) value is incorporated to a shallow depth into warm, moist soil

with a low organic carbon content would produce a high volatilization rate. The rate would be further increased if the relative humidity of the air were low and substantial wind speeds were present, thereby increasing the so-called wick effect (i.e., increasing convective movement of water in the soil to the surface).

Because volatilization is reduced with soil incorporation, the implications of the widespread usage of no-till (NT) farming techniques may mean increased losses of pesticides to the atmosphere in the future. A study by Whang et al. (1993) compared fluxes from side-by-side conventionally tilled (CT) and NT fields for three pesticides. Increased losses from the NT plot compared to the CT plot were observed for all three pesticides. The lowest losses, however, were for atrazine, which is one of the most used herbicides in the country (see table 14) and has an extremely low vapor pressure.

Benjey (1993) has developed a state-by-state estimate of pesticide emissions for twelve major pesticides from eight major crops. The inventory was created using pesticide application data derived from annual county application totals. This information was combined with climatological and crop information, and a volatilization rate for each county for each pesticide, using the Jury (1983) method (see above). Benjey (1993) estimates that emissions equal 20-45% of the amount of pesticide applied, depending on the properties of the pesticide. Table 15 gives partial results from this study. Values are the sum of emissions from Maryland, Delaware, and Virginia for each crop. Although these results are only general estimates, they may give scientists and policymakers some insight into the magnitude of atmospheric sources of pesticides deposited to Chesapeake Bay.

Very few measurements of current-use pesticides in ambient air have been made in the United States, and only one published study is available for Chesapeake Bay. Glotfelty et al. (1990) conducted a study of air and rain concentrations from stations within the Wye River estuary on the Eastern Shore of Maryland. Rain stations were also located in Maryland at Patuxent Wildlife Refuge in Bowie and at Sandy Point State Park near Annapolis. Samples were collected during 1981-82 and were analyzed for alachlor, metolachlor, atrazine, simazine, and toxaphene. The highest levels of these compounds were observed during the spring and summer months. Table 16 shows the mean and range of concentrations in air and rain measured at the Wye River estuary from May to July, 1982.

3.2 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) were used in the United States between 1930 and 1975. During that period, total commercial sales are estimated to have been 570 Gg domestic and 1.4 Gg imported (Durfee et al. 1976). PCBs were released to the environment initially through the manufacturing process and from leaking electrical equipment. After the manufacture and use of PCBs were restricted and essentially eliminated in the late 1970s, the major source for the environment was volatilization and leaching from landfills. Landfills will continue to be an important source to the atmosphere because PCBs volatilize along with anaerobic degradation products (methane and carbon dioxide) (Murphy et al. 1985, Swackhamer and Armstrong 1986). The most important source for the atmosphere currently is the cycling of PCBs through environmental processes. Murphy et al. (1985) estimated that 900 Mg y-1 are released to the atmosphere through

environmental cycling.

Mean total PCB (t-PCB) vapor concentrations in the Chesapeake Bay atmosphere are very similar to concentrations measured at other locations (table 17), but are almost six times lower than those reported over Lake Superior in the summer of 1986 (Baker and Eisenreich 1990). Elevated PCB inventories in the atmosphere over Lake Superior may result from degassing of organic contaminants during the summer months (Baker and Eisenreich 1990). Both the mean concentrations and the congeneric distribution of PCBs in the Chesapeake Bay atmosphere are similar to those recently measured in southern Ontario (Hoff et al. 1992a, 1992b), although the Chesapeake Bay atmospheric fingerprint of vapor-phase PCBs is somewhat more enriched in the higher chlorinated compounds. The annual mean summed PCB concentrations of the PCB congeners common to both studies were 120 and 150 pg m-3 for southern Ontario and Chesapeake Bay, respectively. Vapor-phase PCB patterns do not resemble those found in Chesapeake Bay sediments (Ko and Baker 1994), which show enrichment in the more chlorinated PCBs. This finding is consistent with recent evidence that suggests the burial and removal of the heaviest PCB congeners to sediments and soils are favored, as determined by the congeners Henry s Law constants and octanol water partition coefficients (Swackhamer et al. 1988, Eisenreich et al. 1989, Hornbuckle et al. 1993).

The total PCB wet flux measured in Chesapeake Bay compares well with those measured in other geographic regions (table 17). The measured Chesapeake Bay t-PCB wet flux of 1.9 mimicrog m-2 y-1 is only slightly larger than that reported for rural Minnesota (1.4 microg m-2 y-1 [Franz et al. 1991]), despite a lower volume-weighted mean concentration attributable to greater amounts of precipitation in the Chesapeake Bay region. The t- PCB wet flux to Green Bay, Wisconsin (2 microg m-2 y-1 [Franz et al. 1991]) is very close to the t-PCB wet flux measured in the Chesapeake Bay region.

Polyaromatic Hydrocarbons

Polyaromatic hydrocarbons (PAHs] are formed through the incomplete combustion of fossil fuels or any organic material. PAHs can be released from natural sources such as volcanos and forest fires. However, the primary sources are manmade, and consist of residential wood fires, motor vehicles, industrial power plants, incinerators, and plants where coal and petroleum products are manufactured.

The Chesapeake Bay Atmospheric Deposition Study (CBADS) included the first large-scale experiment to investigate PAHs in the Bay region (Leister and Baker 1994). This experiment made use of four sites. Table 18 compares the average atmospheric PAH concentrations measured at the four CBADS sites (Lewes, Delaware; Elms, Maryland; Haven Beach, Virginia; and Wye, Maryland) with concentrations measured in other geographic regions (Baker et al. 1994). As shown in the table, PAH concentrations in the Chesapeake Bay area are greater than those reported over the remote Isle Royale in Lake Superior (McVeety and Hites 1988), suggesting a small influence of contaminated air plumes in the region encompassing Baltimore and Washington, D.C. With the exception of phenanthrene, the concentrations of PAHs in the air near the Bay are very similar to those measured on the Baltic coast (Broman et al. 1991). There were high levels of PAHs, relative to the Elms site, detected at the several of the sites listed in table 18 (e.g., Haven Beach,

Portland, Baltimore, and Stockholm). These high concentrations are indicative of sites in close proximity to local sources.

Although washout and mixing decrease contaminant concentrations in the atmosphere during transport from urban areas, decomposition of PAHs and other HOCs such a polychlorinated dibenzo[p]dioxins and dibenzofurans via photo-oxidation in the atmosphere also may deplete HOC levels during transport to rural atmospheres (Korfmacher et al. 1980, Webber 1983, Koester and Hites 1992). Nielsen (1988) has demonstrated that the benzo[e]pyrenebenzo[a]pyrene ratio is a diagnostic tool for indicating the rapid decay of benzo-[a]pyrene during tropospheric transport, with the ratio increasing as the air mass travels from the emission source. Simo et al. (1991) report a mean benzo[e]pyrenebenzo[a]pyrene ratio of 0.78 for particles collected over the western Mediterranean. The mean ratio for these two compounds measured at the Elms site (0.71) is slightly larger than the ratio reported by Nielsen (1988) 12 kilometers from an urban area, indicating that the air masses at Elms are probably representative of regional transport of combustion-derived PAHs rather than localized emissions in the vicinity of the site.

Annual wet depositional fluxes of phenanthrene and benzo[ghi]perylene, calculated from precipitation samples collected between June 1990 and July 1991 at the Elms site, are shown in table 19 (Leister and Baker 1994). Measured individual PAH wet fluxes range from 1 micorg m-2 y-1 for dibenz[ah]anthracene to as much as 20 microg m-2 y-1 for pyrene. The values are slightly larger than those reported in the Lake Superior region (McVeety and Hites 1988), probably because of larger regional sources near Chesapeake Bay (e.g., Baltimore and Washington, D.C.). For example, phenanthrene, pyrene, and benzo[ghi]pyrene wet fluxes to Lake Superior are 5.4, 2.3, and 1.3 microg m-2 y-1 , respectively, whereas those in Chesapeake Bay are 9, 20, and 2 microg m-2 y-1 , respectively. However, the PAH wet fluxes for the Chesapeake Bay are lower than those reported in urban areas such as Portland (Ligocki et al. 1985b). Measured PAH fluxes to Commencement Bay in Puget Sound (Puget Sound Water Quality Authority 1991) are large relative to those measured in either the CBADS or Great Lakes studies, which may reflect both proximity of sampling sites to emission sources and the use of questionable sampling procedures in the Puget Sound study.

4. Trace Elements

4.1 Overview

Crustally derived trace elements are generally encountered in the coarse aerosol size fraction (2.5 microm), and are largely removed by dry deposition near their source. Under certain conditions, however, smaller particles of resuspended soil may be transported over long distances (thousands of km), which is why outbreaks of Saharan dust are regularly observed in South Florida.

Trace metals are those elements that are not primary components of crustal rocks. Usually

included in this category are transition metals that are moderately rare in the environment, such as iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn). These elements are essential for life in minute quantities, but exhibit adverse toxic effects at higher concentrations. Other trace metals that are quite rare in the environment, such as cadmium (Cd), mercury (Hg), lead (Pb), selenium (Se), and arsenic (As), are considered hazardous, particularly for aquatic organisms. Such elements are classified as Priority Pollutants by the EPA, and many are designated as Toxics of Concern for the Chesapeake. As some of these elements (e.g., As, Se) are not true metals with respect to a strict chemical definition, the term trace elements is often employed to more accurately describe them.

Atmospheric trace elements are derived from both natural and anthropogenic sources. Natural sources include soil resuspension, volcanism, and forest fires. Human sources include high- temperature combustion processes, including the burning of fossil fuels for electric power generation, ore smelting/refining, refuse/sludge incineration and transportation. Atmospheric trace metal emission inventories (Galloway et al. 1982, Nriagu and Pacyna 1988, U.S. Environmental Protection Agency 1991a) indicate that human activities are the dominant sources of most elements, particularly in industrialized regions such as the eastern United States.

As many trace metals are co-emitted from these processes along with oxides of sulfur and nitrogen, there exists a potential for the significant atmospheric mobilization and deposition of other elements in acid precipitation that may have equally important ecological implications. In fact, a positive correlation has been shown to exist between the acid anions in precipitation (SO_4^{-2} and NO_3^-) and elemental tracers of coal combustion (Se and As) (Cutter and Church 1986, Scudlark and Church 1988).

During high-temperature combustion processes, trace metal oxides are vaporized and subsequently condense on or form fine, submicron aerosols (Smith et al. 1979, Natusch et al. 1974). Thus, most atmospheric trace metals exist in association with small particles, although some (e.g., Hg, Se) exhibit significant vapor-phase components. In terms of atmospheric deposition, such size fractionation is important because submicron aerosols (a) are least efficiently removed by pollution control devices, (b) are typically injected into the atmosphere above ground level by smokestacks, and (c) have relatively long atmospheric residence times (days or weeks), rendering them susceptible to long-range transport. Consequently, atmospheric trace element emissions impacting the Chesapeake may originate a considerable distance upwind, so that the Chesapeake airshed encompasses an area much larger than the Bay s watershed.

Owing to the extremely low concentrations of trace metals in the atmosphere, the accurate determination of trace metal concentrations presents a challenge in terms not only of performing accurate analyses but also of obtaining a representative sample free of contamination. In fact, recent reviews of the historical data on the concentration of trace elements in precipitation (Galloway et al. 1982, Barrie et al. 1987, Nriagu 1992) cast considerable doubt on the reliability of much of the previously published data and the efficacy of the analytical and sample handling techniques utilized. In many instances, the data have been compromised by both analytical shortcomings as well as the failure to observe the requisite ultra-clean trace metal protocols (Ross 1986, Chan et al. 1983).

4.2 Evidence of Deposition

The first successful attempts to measure trace elements in the atmosphere using rigorous procedures were done over the ocean in conjunction with the Sea-Air Exchange (SEAREX) Program (Duce et al. 1976, Arimoto et al. 1985, 1987, 1990). Initial SEAREX results over the Atlantic drew attention to the hypothesis that atmospheric deposition can be an important, if not dominant, source of trace elements for oceanic surface waters. It was subsequently demonstrated that atmospheric deposition of trace elements to the Sargasso Sea (Jickells et al. 1984, Church et al. 1984) dominates the inputs to and flux from the ocean water column (Jickells et al. 1987). Considerable attention and scientific debate has been focused on recent work by Martin and co- workers (e.g., Martin and Fitzwater 1988), which indicates that the input of atmospherically derived trace element micronutrients such as Fe may limit primary pro- duction in stratified oligotrophic waters. The far-reaching implication of this hypothesis is that atmospheric deposition may constrain a major sink of atmospheric CO2, the primary greenhouse gas.

The importance of atmospheric deposition has also been established for coastal and inland systems (Patterson and Settle 1987), including the Baltic, Mediterranean, and North Seas (Jickells et al. 1989), as well as on a global scale (Duce et al. 1991). In fact, the levels of trace elements in precipitation have been shown to exceed the dissolved concentrations in many surface waters (Nriagu and Pacyna 1988). Furthermore, the atmospheric input of trace metals has been estimated to equal or exceed riverine loading to the world oceans (Nriagu 1992).

Atmospheric deposition appears to be highly episodic for both wet and dry deposition. For example, it has been shown (Scudlark and Church 1994a) that on the mid-Atlantic coast, 10% of the most prominent precipitation events can account for one-third of the total nitrogen wet deposition. Similarly, for dry deposition, a small fraction of periods with high turbulence can lead to episodes of intensified deposition. Wu et al. (1994) suggest that owing to the disparity between deposition velocities for different wind speeds, the deposition associated with a wind speed of 20 m s-1 for 10 minutes a day would be equivalent to the deposition associated with an entire week at an average wind speed of 5 m s-1. Such episodicity may have major implications in terms of ecosystem response, and in some instances, may be more important than the cumulative loading.

The longest continual record of trace element wet deposition has been made at Lewes, Delaware, by the University of Delaware. Wet deposition has been collected on an event basis at a site near Cape Henlopen on the mid-Atlantic coast since 1982 (Church et al. 1984, Church and Scudlark 1992). The success of this record has come from the development of suitable clean collection/handling protocols and sufficiently accurate and sensitive analytical techniques developed specifically for trace elements in precipitation (Tramontano et al. 1987, Scudlark et al. 1992).

The data from Lewes show that the wet-depositional fluxes of most trace elements have been relatively constant over the past decade. The notable exception is the sixfold decrease in the Pb concentration (figure 4), which closely parallels the estimated decrease in the atmospheric Pb burden over this period in response to phasing out of alkyl-Pb gasoline additives (Eisenreich et al. 1988).

As is also the case with nitrogen and organic contaminants, there do not exist widely accepted methodologies for measuring trace metal dry deposition by direct means. The standard practice is to measure aerosol concentrations and to calculate dry flux by utilizing representative deposition velocities. The dry deposition at Lewes has been estimated accordingly (Church and Scudlark 1992), apportioning the crustal component based on typical soil composition for the eastern United States (Taylor and McLennan 1985), using aluminum (Al) as a crustal normalizer. The crustal fraction is assigned a deposition velocity that is typical of mineral aerosols (0.3 cm s-1), and the noncrustal fraction is assigned a deposition velocity typical of accumulation mode aerosols (0.1 cm s-1) (Lin et al. 1994). A quantitative comparison of atmospheric wet and dry deposition (figure 5) indicates that the proportion of dry deposition for the crustal elements (i.e., Al, Fe) appears to be greater than that of wet deposition; however, for those elements that are most anthropogenically mobilized and most toxic (i.e., Zn, Cd), wet deposition appears to provide an equal or greater mode of atmospheric removal. For both wet and dry flux, the crustal contribution appears to be minor for most elements.

Compared with fluvial trace element inputs to the Delaware Bay, atmospheric deposition has been estimated (Church and Scudlark 1992) to be a small, albeit significant, source for a number of elements (e.g., Cu, Zn). However, because trace elements are efficiently scavenged by estuarine removal processes, atmospheric deposition to the contiguous shelf waters of the Mid-Atlantic Bight appears to furnish a major and, in some instances, dominant contribution (Scudlark and Church 1994b). For example, as shown in figure 6 , particle-reactive elements such as Fe and Pb are predominantly trapped within the estuary, so that atmospheric deposition provides a comparatively large contribution to coastal shelf waters. Conversely, a large fraction of the biochemically reactive elements (e.g., Cd, Cu) survives transport to the shelf as robust organic complexes; consequently, the relative atmospheric input of these elements to the bight is minor.

Measurements of atmospheric trace element deposition to Chesapeake Bay are limited. Indirect evidence is provided by the excess Cu, Pb, and Zn in surface sediments of the Bay, which has been attributed to atmospheric deposition (Helz et al. 1985a, 1985b). In a one-year study in the early 1980s, Wade and Wong (1982) and Conkwright et al. (1982) reported measurements of precipitation trace element concentrations at four sites in the lower (Virginia) Bay and six sites in the upper (Maryland) Bay. Several of these sites were in close proximity to the CBADS sites described below. Although only concentrations were reported, it is possible to infer wet-depositional fluxes from these data.

The CBADS provides the most comprehensive evaluation of trace element deposition to Chesapeake Bay to date. The CBADS was a three-year (June 1990 to September 1993) effort that had four primary objectives(1) to accurately measure the concentration of selected trace elements and organic contaminants in precipitation and atmospheric aerosols, (2) to determine the temporal and spatial variability in precipitation concentrations and fluxes, (3) to evaluate the relative magnitude of atmospheric depositional fluxes (wet versus dry), and (4) to estimate the atmospheric fluxes of contaminants (trace metals and synthetic organic compounds) to the surface of the Bay. In conjunction with the CBADS, 11 trace elements (Al, As, Cd, Cr [chromium], Cu, Fe, Mn, Ni, Pb, Se, and Zn) were measured in the ambient atmosphere and precipitation at four

sitesWye, Maryland; Elms, Maryland; Haven Beach, Virginia; and Lewes, Delaware.

Preliminary results of the CBADS (Baker et al. 1993b, 1994, Scudlark et al. 1994a, Wu et al. 1994) indicate that, except for Al and Fe (and to a minor extent Cr and Mn), most trace element deposition to Chesapeake Bay is of noncrustal, presumably anthropogenic origin. The CBADS data also reflect seasonal trends in wet and dry deposition (characterized by a summer maximum) for certain elements (e.g., Cd, Pb, Zn). For some elements, distinct north-to-south concentration gradients are evident, consistent with the emission source distribution.

The CBADS data indicate a high degree of spatial and temporal variability for wet deposition; however, the aerosol trace element concentrations do not reflect the same degree of intersite variability. In general, the highest aerosol concentrations for the anthropogenic elements are encountered during periods of low winds and temperature inversions (i.e., air mass stagnation), while concentrations decrease during scavenging episodes such as high winds and precipitation. Conversely, the concentration of crustal elements increases during periods of high winds or soil-resuspending activities (e.g., agricultural and construction activities), particularly during periods of low soil moisture or snowcover.

Compared with estimated fluvial loading, the CBADS results support the hypothesis that atmospheric deposition is an important source of trace element contaminants in the Bay. For example, as shown in figure 7, the atmospheric inputs of Cd and Pb are comparable to those provided by riverine sources (Scudlark et al. 1994b). However, the quantitative understanding of trace element flux from other potentially important sources (e.g., urban runoff, groundwater input, shelf exchange) is currently insufficient to allow for evaluating atmospheric deposition in a mass-balance framework.

In figure 8, the atmospheric wet fluxes of trace metals determined in the CBADS are compared with fluxes reported in the other studies previously noted, as well as in two other recent studies that similarly addressed atmospheric deposition to coastal waters. One of the recent studies is the Great Lakes Atmospheric Deposition (GLAD) Network, established by the EPA in 1981 and initially consisting of 35 collection sites in the United States and Canada. Wet fluxes were calculated from the arithmetic average precipitation concentrations reported at 13 rural sites for the period 1982-89 (Klappenbach, pers. comm.), and assumed an annual average precipitation of 100 cm y-1. The other recent study is an EPA-sponsored study in Puget Sound (U.S. Environmental Protection Agency 1991b), consisting of five sites. Wet fluxes plotted are the average reported at two sites identified as background, presumably representative of incident clean Pacific air. In contrast to the other data plotted, the Puget Sound data represent total (wet + dry) atmospheric deposition.

In comparing results in figure 8, it should be noted that not all elements were determined in all studies. For most of the anthropogenically derived elements (notably Pb, Ni, Zn, Cd, and Cu), the long-term average fluxes measured downwind at Lewes were somewhat higher than the CBADS average. For Pb, this is not an unanticipated result, owing to the aforementioned transient (decreasing) Pb signal, which would bias the average concentration, which incorporates the earlier Lewes data. However, for the other elements,

the apparent larger fluxes observed at Lewes are enigmatic, considering the lack of major emission sources over Delmarva. One plausible hypothesis is that the apparent heightened deposition at Lewes is attributable to unique micrometeorological or scavenging conditions (e.g., nucleation by sea salt aerosols) associated with the coastal marine boundary layer. In fact, synchronous measurements of precipitation events at Chesapeake Bay shore and ship-based sites support this theory (Baker et al. 1994).

The earlier Chesapeake Bay data sets (Wade and Wong 1982, Conkwright 1982) are also not in accord with the contemporary CBADS results (Baker et al. 1994). Except for the crustal elements (Al, Fe, and Mn), the trace metal concentrations reported in the earlier studies were generally a factor of 2-6 higher than the more recent data. If these differences are authentic, it would suggest that precipitation concentrations have decreased dramatically over the past decade. However, this conclusion is not supported by the contemporaneous record at Lewes, which does not indicate any abatement (except for Pb, as previously discussed).

The wet fluxes inferred from the GLAD data are similar to the CBADS results for some elements (e.g., Cu, Mn, Ni), but not others (e.g., Pb, Zn). Given the differing emission sources that affect the Great Lakes, such differences are not surprising. The Puget Sound fluxes are considerably larger than even the highest estimates of total (wet + dry) fluxes reported for Chesapeake Bay, and are significantly greater than would be expected for clean background sites (Nriagu 1992). Thus, either the sites were not truly background or the elevated depositions reflect sampling/analysis artifacts.

Recent studies have addressed the sources of atmospheric contaminants in the Chesapeake region using receptor models (Gordon et al. 1994, Scudlark et al. 1994a). One noteworthy observation is that, for the mid-Atlantic region, wet deposition associated with transport from the southeastern United States is comparable to that derived from the traditionally implicated midwestern source region (e.g., the Ohio River valley). Furthermore, demographic considerations suggest that in the future, the relative southeastern contribution will increase as the northern Rust Belt industries decline while the Sun Belt region continues to industrialize.

One of the major uncertainties associated with estimation of atmospheric contaminant input to estuaries such as the Chesapeake is in gauging the indirect atmospheric component derived from watershed transmission. Based on very limited published data (Lindberg and Turner 1988), the landscape throughput of trace elements appears to be quite small (

5. Key Steps to Improve Quality of Estimates of Atmospheric Loadings of Nitrogen and Contaminants to Chesapeake Bay

Depending on chemical species, the current uncertainties in estimates of atmospheric loading of nitrogen and contaminants to Chesapeake Bay and its watershed range from + or - 20% to orders of magnitude. However, if ways are to be found to reduce such atmospheric deposition, it is essential that the processes be better understood and that the quality and reliability of the estimates be improved. Accordingly, it is recommended that

the following steps be initiated (these steps are not comprehensive or specific suggestions, but a list of key areas of uncertainty that can serve as discussion points in future deliberations)

- **Conduct monitoring and research experiments focused on improving measurements and modeling techniques to further understand and quantify the emission cycles of the key chemical species.**
- **Develop and perform nitrogen speciation experiments, including experiments on organic nitrogen and ammonia compounds. Subsequently, conduct intensive studies of the dry deposition rate nitrogen compounds from air crossing the watershed zone of the Chesapeake Bay region.**
- **Investigate the effect of localized contaminant deposition in both urban and near-urban environments. Specifically, develop estimates of surface water loadings attributable to urban runoff, and investigate the temporal and spatial distribution of NOy deposition.**
- **Establish integrated monitoring sites of atmospheric deposition and emission. The initial focus should be the concurrent measurement of the chemistry, intensity, and duration of precipitation and streamflow events.**
- **Establish over-water precipitation chemistry sites and compare the results with those from land-based precipitation chemistry sites.**
- **Establish common data bases to process and store data that can be used as input to models and/or to test specific predictions of the models. This effort should include emission inventories (anthropogenic and natural), wet and dry deposition rates at specific locations to be covered by the model, spatial distributions of soil and atmospheric moisture, chemical concentration distributions, and relevant meteorological supporting data.**
- **Clarify the role of urban areas as a source of atmospheric contaminants in surface waters. Conduct research on sampling methods for small particle deposition and source attribution for organic contaminants.**
- **Investigate the bioavailability of materials deposited from the atmosphere. Conduct exposure studies to learn how chemical speciation influences exposure.**

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Mineralizaiton and Availability of Nitrogen in Organic Waste-Amended Mid-Atlantic Soils

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Introduction

Pollution resulting from animal production has been a key issue in the mid-Atlantic states since the early days of the Chesapeake Bay nonpoint-source programs.

Animal manures and biosolids (human wastewater treatment sewage sludge meeting biological and chemical criteria that permit land application) can have both beneficial and detrimental effects when applied to agricultural land as a means of recycling organic matter and nutrients and disposing of unwanted wastes. When applied properly, organic wastes can furnish nitrogen (N) to enhance soil productivity and be disposed of safely. When applied improperly, however, they can load excessive amounts of N to both groundwater and surface water (Bouldin et al. 1984) and pose a threat to the environment and to the health of both humans and livestock.

Animal manures and biosolids are composed of both inorganic (mineral) and organic forms of N. Inorganic forms of N such as ammonium (NH_4^+) and nitrate (NO_3^-) are readily available for plant uptake, but organic forms of N must mineralize, or decompose, to inorganic forms prior to utilization by plants.

Mineralization is not a uniform process. Rather, it can vary greatly as a result of the heterogeneous nature of the manures and biosolids and the differing mineralization rates of the individual forms of N. Therefore, it is often difficult to make an accurate determination of the amount of plant-available N in the organic forms of N in manures and biosolids.Consequently, the unpredictability of mineralization rates, combined with a lack of uniformity in the practice of spreading manures and biosolids, can lead to the accumulation of excess amounts of inorganic N in the soil.

Excess levels of soil inorganic N may be transported to groundwater or surface water. Nitrate is mobile in the soil and is easily transported to groundwater and surface water by deep leaching, shallow subsurface flow, or surface runoff (Hallberg 1987). The land application of manures and biosolids is one of the chief sources of nitrate contamination of groundwater (Fletcher 1991). Ammonium may move into surface water with eroded soil particles or as a result of runoff (Foster and Neibling 1986).

High concentrations of nitrate in drinking water pose hazards to humans upon bacterial conversion of ingested nitrate to nitrite (NO_2^-) within the digestive tract. Nitrite can induce methemo-globinemia (a reduction in the oxygen- carrying capacity of the blood) in infants (Council for Agricultural Sciences and Technology 1985). Nitrite also can react with other substances, such as amines, to form N-nitroso compounds, which have been shown to induce tumors in laboratory animals (Crosby and Sawyer 1976). Concentrations of nitrate-

N that do not exceed the U.S. Public Health Service standard of 10 mg/l are assumed to be safe for human consumption.

Nitrite toxicity may be induced in livestock consuming high levels of nitrate in water or feed. Chronic nitrite poisoning in livestock produces anorexia, vasodilation, lowered blood pressure, abortion, and reduced lactation (National Research Council 1978). A water quality standard of 100 mg (NO3-)-N/l has been suggested for livestock (University of Wisconsin Extension 1983).

The major environmental problem associated with N enrichment in Chesapeake Bay is eutrophication. This process results in the excess production of algae and phytoplankton and, as these organisms die and sink, oxygen depletion occurs in the lower depths of the Bay (Gillelan and Macknis 1983).

It should be noted that the application of sewage sludge to agricultural lands (croplands, pastures, and forestlands) is increasing as a disposal practice in lieu of such environmentally unsound and expensive methods as landfill disposal, incineration, and ocean dumping. However, the practice is stringently regulated, is usually undertaken as part of a well-designed, site-specific nutrient management plan, and involves the use of agronomic rather than disposal rates of application. Nevertheless, as with manures, the difficulty in predicting N mineralization rates and in spreading the wastes uniformly provides a similiar potential for water contamination (Brockway and Urie 1983, King et al. 1977, Sommers and Giordano 1984).

It is essential that N loadings to the waters of the Chesapeake Bay system be reduced in accordance with the goals set in the second Chesapeake Bay Agreement signed in 1987 by the District of Columbia, Maryland, Pennsylvania, and Virginia. The goal set for nutrient reduction called for a 40% reduction of the controllable N and phosphorus (P) loadings to the Bay between the years 1985 and 2000.

A key factor in achieving this goal will be to develop and implement a standardized approach to the management of organic wastes in the mid-Atlantic region, with emphasis on the use of agronomically reliable and environmentally sound mineralization rates for N and application rates for manures and biosolids.

This paper begins with an overview of the general factors associated with the nitrogen cycle and the characteristics of manures and biosolids. It then summarizes current practices used in the mid-Atlantic states to estimate N mineralization and predicted plant-available N rates, and it concludes with a recommended approach to the N management of organic wastes.

1.1 Glossary of Terms and Abbreviations

Activated sludge process: **Removal of organic matter from sewage by saturating it with air and adding biologically active sludge.**
Aerated lagoon: **A lagoon or pit containing raw wastewater. Air is mixed into the wastewater to achieve secondary wastewater treatment.**
Aerobic digestion: **Decompostion of organic matter by microorganisms in the presence of molecular oxygen.**

Agronomic rate: **Addition of organic waste to a soil at a rate that meets the fertility requirements of the crop for that particular soil. Such a quantity of waste would not tax the soil's ability to assimilate the waste or contribute to environmental degredation.**
Ammonia: **Gaseous compound of nitrogen and hydrogen (NH3).**
Ammonia volatilization: **Gaseous loss of nitrogen to the atmosphere in the form of ammonia.**
Ammonium: **Ionic compound of nitrogen and hydrogen that is available for uptake by plants (NH4+).**
Anaerobic digestion: **Decomposition of organic matter by microorganisms in the absence of molectular oxygen.**
Biosolids: **Municipal wastewater sewage sludge beneficially applied to the land.**
Carbon/nitrogen (C/N) ratio: **The raio of the weight of organic carbon (C) to the weight of total nitrogen (N) in a soil or organic material.**
Compost: **Organic residues that have been piled, moistened, aerated, and allowed to undergo biological decomposition.**
Denitrification: **The biochemical transformation of nitrate or nitrite to nitrogen gas.**
Digestion: **Decomposition of sewage sludge resulting in partial gasification, liquefaction, and mineralization of pollutants.**
Eutrophication: **The normally slow aging process by which a lake evolves into a bog or a marsh and ultimately assumes a completely terrestrial state and disappears. During eutrophication, the lake becomes so rich in nutritive compounds , especially nitrogen and phosphorus, that algae and other microscopic plant life becomes superabundant, thereby choking the lake and causing it eventually to dry up. Eutrophication can be accelerated by many human activities.**
Groundwater: **The body of water beneath the ground surface int he zone of saturation, consisting primarily of water that has seeped down fromt he surface.**
Immobilization: **Transformation of inorganic nitrogen compounds into and organic form. This process is accomplished by soil organisms that assimilate inorganic nitrogen compounds and transform them into their cells and tissues.**
Leaching: **The removal of materials in solution from the soil by percolating waters or other liquids.**
Mineralization: **Transformation of nitrogen from an organic to an inorganic form. This process is facilitated by heterotrophic organisms that use nitrogenous organic compounds as energy sources.**
NH4-N: **Chemical symbol for nitrogen when present in the form of ammoninum (NH4+).**
Nitrification: **The biochemical transformation of ammonium to nitrate.**
NO3-N: **Chemical symbol for nitrogen when present in the form of nitrate (NO3-).**
Plant-available nitrogen: **The nitrogen that is available for uptake by a plant. This generally includes nearly all of the inorganic nitrogen plus a fraction of the organic nitrogen that is expected to become plant available through mineralization.**
Potentially mineralizable nitrogen: **The forms of organic nitrogen that, by the nature of their composition, may undergo mineralization during a defined time period.**
Primary sludge: **The raw sludge obtained from the primary stage of a wastewater treatment plant by collecting, floating, and settling solids.**
Primary wastewater treatment: **The stage in basic treatment for removal of the material that will float or settle in sewage. It is a physical process accomplished by (1) using screens to**

catch coarse solids and (2) settling tanks.
Runoff: **The portion of the precipitation on a drainage area that is discharged from the area in stream channels. Types include surface runoff, groundwater runoff, and seepage.**
Secondary sludge: **The solids removed by settling in sedimentation tanks follwing biological treatment.**
Secondary wastewater treatment: **The second step in most wastewater treatment systems in which bacteria digest the organic parts of the wastes. The digestion is accomplished by bringing the sewage and bacteria together in trickling filters or in an activated sludge process.**
Sludge: **The solid matter that settles to the bottom, floats, or becomes suspended in sedimentation tanks and must be disposed of by filtration and incineration or by transport to appropriate disposal sites.**
Stabilized sludge: **Primary and activated sludge that has been decomposed into a relatively inert material.**
Total Kjeldahl nitrogen: **The total amount of nitrogen present in organic samples such as soil organic matter and sludge as determined by the Kjeldahl technique.**

2. Nitrogen Cycling in Organic Waste-Amended Soils

2.1 General Factors

The supply of plant-available N in the soil is determined not only by the process of mineralization but also by the process of immobilization, whereby, as soil microbes multiply, they assimilate inorganic N compounds and transform them into organic forms of N that cannot be utilized by plants (immobilization). Mineralization and immobilization work in opposite directions by building up and breaking down organic matter. The supply of N is determined by the additive effects of the two processes and is expressed as either net mineralization or net immobilization. Thus, the change in soil inorganic N upon the addition of animal manures or biosolids to soil is a function of the competition between mineralization and immobilization processes, and any increase in soil inorganic N is a result of net mineralization. Mineralization and its related processes constitute the N cycle (see figure 1), an essential component of the Earth's biological cycles.

Many factors determine the amount of plant-available, or inorganic, N mineralized from organic wastes applied to the soil. Direct factors include waste composition, application and/or incorporation method, and application timing. Indirect factors include environmental influences on mineralization, such as climate (temperature and moisture amounts and patterns) and soil properties. Soil pH, salt content, concentrations of toxic chemicals and heavy metals, and the effects of fertilizers, herbicides, and pesticides may reduce mineralization by inhibiting microbial activity. Physical conditions such as waterlogging and compaction of soil may hamper microbial activity by reducing aeration. Wetting and drying, as well as freezing and thawing, may reduce mineralization by diminishing microbial viability or may enhance mineralization by increasing the availability of potentially mineralizable N to microbes.

Generally, it is the ratio of carbon (C) to N in the material undergoing mineralization or immobilization and in the soil to which the waste is applied that have the greatest effects on

these N transformations. When the C/N ratio of the waste is less than about 20-25, mineralization of organic matter yields more N than required by the microbial biomass for protein, and the net result is an addition of inorganic N to the soil pool. When the C/N ratio of the waste is greater than about 30, more N than contained in the mineralized organic matter is required by microbes for protein production. Microbes will obtain additionally needed N from the existing soil inorganic N pool, resulting in a net immobilization of soil N. Animal manures, biosolids, and legume crops generally have C/N ratios of between 5 and 25 and are net mineralizers of N. Straw, mature small grain crops, tree leaves, and wood chips have C/N ratios that range from 30 to greater than 1,000, and are net immobilizers of N. The total amount of nitrogen mineralized should be influenced by the C/N ratio of the waste, not the soil, because the C/N ratio of native soil organic matter is 10 (Brady 1974) and probably exerts little control over the total amount of decomposition of applied waste.

Soil temperature and moisture strongly affect mineralization because of their influence on biological activity. The populations and activity of heterotrophic, N-mineralizing suites of microorganisms respond to temperature and moisture optima. Therefore, variations in mineralization of soil-applied organic wastes and subsequent plant-available N largely are a function of the composition of the waste, application methods and timing, climatic region, and soil properties.

The concept of a "decay" series has been developed by Pratt et al. (1973) to describe the gradual decomposition of organic N and release of inorganic N with time. This concept recognizes that organic N is gradually mineralized over several years and assigns decreasing mineralization rates to various organic wastes. For example, a decay series of 0.5, 0.2, 0.1, and 0.05 indicates that 50% of the initial total N mineralizes during the first year, 20% of the N remaining after the first year mineralizes during the second year, 10% of the N remaining after the second year mineralizes during the third year, and 5% of the N remaining after the third year mineralizes during the fourth year. The mineralizable N may be expressed as either a fraction of total (organic and inorganic) N or only organic N. The decay series concept and its elaborations far exceed the experimental data available for their quantitative verification; however, they do provide a logical framework for more experimental work and for summarizing available data.

The mineralization series as formulated by Pratt et al. (1973) does not account for leaching, denitrification, and ammonia (NH_3) volatilization losses once mineralization has occurred. Hence, plant uptake, the ultimate objective of using organic waste to supply nutrients, is one step removed from the mineralization series. Decay series values are often adjusted downward to reflect estimated losses (Gilbertson et al. 1979).

2.2 Relevant Characteristics of Manures and Animal Wastes

Animal manure is a mixture of metabolic products such as urea and uric acid, living and dead organisms, and residues from the original feed (Wilkinson 1979). Variations in N content and N availability occur because of dietary and metabolic differences among types of animals. The processing, handling, and storage of animal manures influence the transformations of N compounds, which result in differences in mineralization potential. Only about half of the total N originally present upon excretion remains in the insoluble organic forms after short periods of storage.

Ammoniacal forms of N are found in solution and are easily lost in drainage water and through NH3 volatilization. Volatilization of ammonia is the major initial loss pathway of N from manures (Hoff et al. 1981, Lauer et al. 1976, Reddy et al. 1979b). Safley et al. (1986) reported a 23% loss of N from dairy manure from the time of excretion onto the barnlot until removal from storage. Most of the loss occurred during the 24-hour period between barnlot cleanings. Ammonia volatilization losses of N from various animal manure handling and storage operations has been reported to range from as little as 3% to as much as 80% (Burns et al. 1985, Lauer et al. 1976, Muck and Richards 1983, Muck et al. 1984, Pratt and Castellanos 1981, Westerman et al. 1983).

Nutrient analysis of animal manures is performed by public and/or private laboratories in every state in the mid-Atlantic region and should be utilized for manure rate recommendations. Examples of the nutrient content of manures are provided by Barker (1980). Dairy, beef, and swine averaged 6 kg total N per 1,000 kg of fresh manure. The amounts of N per 1,000 kg of poultry manure, measured at 14 kg for caged layer, 18 kg for dry turkey litter, and 26 kg for dry broiler litter, are higher than in other livestock wastes. The variations in the nutrient contents of animal manures are too great to permit the use of an average value for the calculation of nutrient loading rates. In the absence of a manure nutrient test, suggested manure application rates must rely on general and, probably, inaccurate estimates of the forms and amounts of C and N. Descriptions of the manure types associated with beef cattle, dairy cattle, swine, and poultry are presented in table 1.

2.3 Relevant Characteristics of Biosolids and Sludges

The composition of biosolids varies greatly. The characterization of municipal sludges from 45 sites in seven southern states showed enormous variability in nutrient composition (King et al. 1986). The total N concentration of the solid fraction ranged from 0.6% to 7.5% and median N concentration was 3%. Sommers (1977) found even a greater range of total N, from