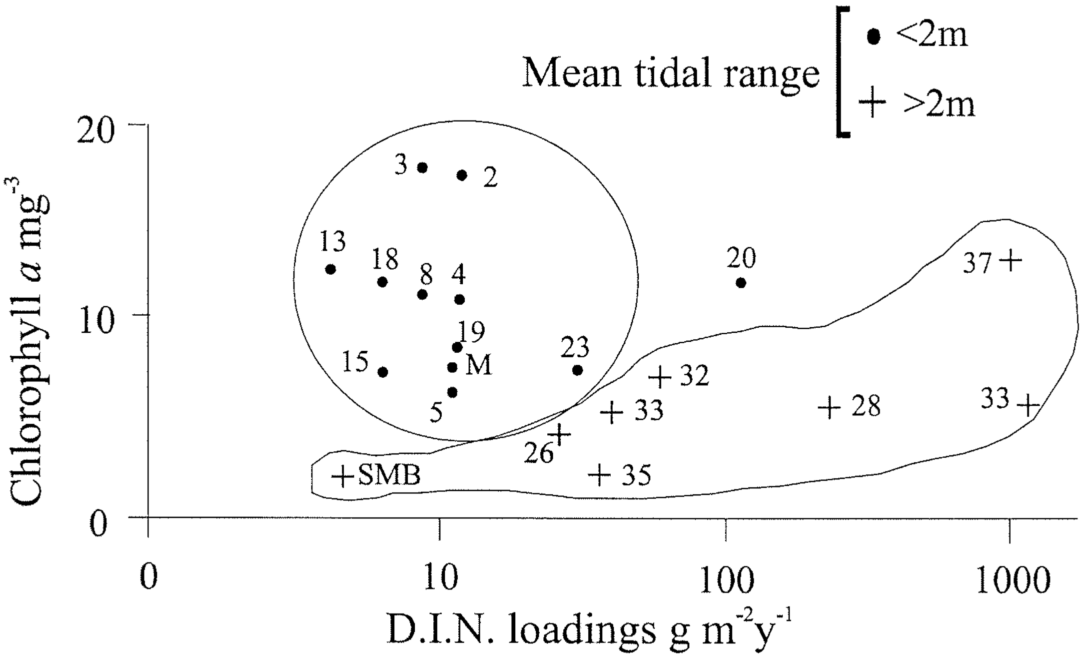

Figure 3-2a. Relationship between the mean annual loadings of dissolved inorganic nitrogen (DIN) and the mean annual concentration of chlorophyll *a* in microtidal and macrotidal estuaries.

Summary

Various ways are available to classify estuaries regarding their vulnerability to nutrient enrichment. None appear to provide all the information a resource manager may want for decisionmaking. The NOAA estuarine export potential (EXP) appears to have the current greatest utility for predictive purposes for large systems, but even this approach embodies considerable variability (e.g., see Figures 6-5 and 6-6 in NRC 2000). For embayments within a larger estuary, the comparative empirical modeling approach has been demonstrated to have considerable utility. The more theoretical models eventually may provide greater predictive power, especially as to biological sensitivities to nutrient enrichment. They are data intensive and may become more useful at a future time.

3.4 COASTAL WATERS SEAWARD OF ESTUARIES

Several approaches are available to classify coastal waters. The geomorphic focus is a good place to begin, hydrographic considerations should follow, and finally habitat and community features should be considered. Although functional considerations and theoretical indices are not described for coastal waters, they have as much relevance for these waters as they do for estuaries. Even though much of the concern for coastal waters will be within 20 nautical miles of shore, and most of that within the 3-mile limit, elements of the following large-scale classification scheme will have value to the manager and investigator.

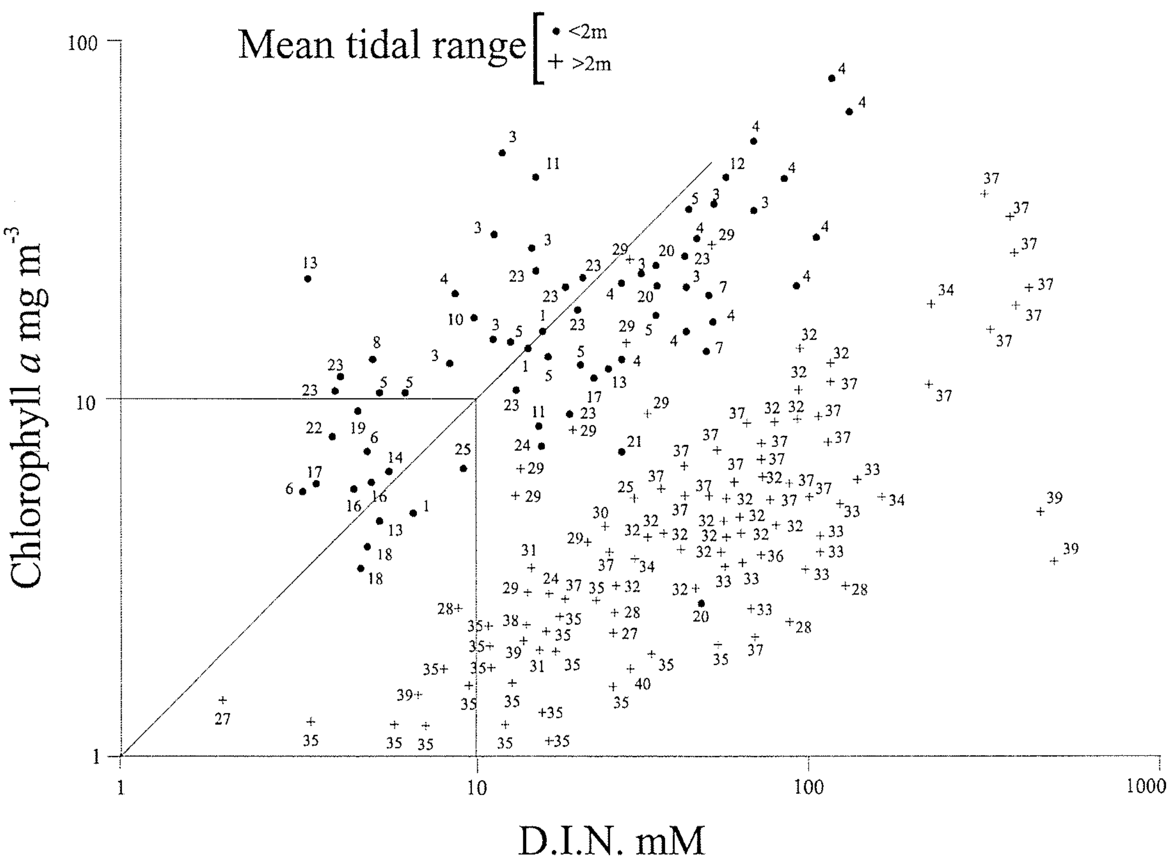

Figure 3-2b. Relationship between the mean annual concentrations of dissolved inorganic nitrogen (DIN) and chlorophyll *a* in microtidal and macrotidal estuaries. Source: Monbet 1992.

Geomorphic Classification

The flow of energy and nutrients through coastal food webs differs greatly among continental shelves, and is driven largely by differences in the form and amount of primary production (e.g., seagrasses are important in the Big Bend area of Florida and kelp forests are important habitats along much of the U.S. Pacific Coast and sections of coastal Maine). These differences in turn ultimately are determined by differences in local and ocean-scale patterns of climate (e.g., light and temperature effects), water circulation, chemistry, and shelf geomorphology (Alongi 1998). The spring bloom, especially along the U.S. Atlantic Coast, generally progresses from low to higher latitudes but with sharper seasonal peaks toward higher latitudes. Variability in the progression should be considered in any classification scheme. Because near-coastal shelf oceanographic processes usually are not limited by the jurisdiction of a single State, it is important that a similar classification approach be shared among coastal States, where that oceanography determines the sensitivity of the ecosystem to nutrient enrichment. The geographic extent of the shelf in which a State has jurisdiction is a useful place to begin classification. Here one should consider whether the shelf is wide or narrow (e.g., mid-Atlantic versus Pacific Coast). The Texas coastal shelf is very wide, with a gentle slope compared with much of the northern Gulf of Mexico. The steepness of the slope is another useful factor, as it may influence bottom sediment stability and upwelling. The degree of bottom roughness or sculpture may influence vertical mixing, which may in turn influence water column stability and depth of the euphotic zone versus mixing depth.

Nongeomorphic Classification

Walsh characterized the world's continental shelves on the basis of their location, major rivers, and rates of primary production, and included some U.S. coastal waters for comparison. The shelf proper is where oceanic and estuarine boundaries often intermingle. At the shelf edge, cold, nutrient-rich water and associated materials intrude onto the shelf. There, exchanges often are rapid, promoting conditions favorable for higher fertility than in the open ocean. Higher primary productivity is the main reason why approximately 90% of the world's fish catch is harvested on the continental shelves versus the open sea (Alongi 1998).

Water Quality Trend Detection on the Shelf

Physical mixing and advective processes may add considerable variability to water column measures. Therefore, it is important to consider detection of trends in nutrient concentrations and measures such as chlorophyll *a* based on comparisons at a reference salinity (e.g., 30 psu). Otherwise, classification schemes may incur extraneous variability. A common approach is to use "mixing diagrams" to compare measured changes in an ambient constituent among sampling periods. At mid- and higher latitudes, winter measures of DIN and DIP may provide insight into long-term trends of changes in nutrient concentrations available to drive the spring bloom. At low latitudes winter values will likely have less applicability, as primary production has a smaller seasonal signal.

Presence of Large Rivers

Although large rivers are included in Walsh's characterization of shelf systems, it seems useful to distinguish shelf areas based primarily on large rivers, such as the Mississippi River in the Gulf of Mexico and the Columbia River off the Washington-Oregon coast. Large rivers on the shelf dominate local ecological relationships.

Hydrographic Features

Vertical salinity differences tend to decrease toward the open ocean boundary. The principal reason is summertime thermal stratification. The thermocline tends to be deeper toward the open sea margin, except where buoyancy effects are associated with large rivers that flow onto the shelf. Coastal waters contain a variety of biotic communities, including a diverse assemblage of macroepifauna and -infauna, kelp forests, coral reefs, bottom and pelagic fishes, marine mammals, and seabirds. The relationship of these communities to physical-ordering factors can assist in classification.

Temperate and subtropical coastal waters also experience a seasonal sea-level fluctuation, whereby summer levels rise approximately 0.2 m by upper-ocean heat expansion, producing what is known as thermosteric effects (Pattulo et al. 1955, Bell and Goring 1998). This nontidal process operates in conjunction with other factors affecting apparent mean sea level (e.g., near and far-field wind effects and barometric pressure). Depending on local conditions, water levels overlying the continental shelf and in estuaries can rise from 0.1 to 0.2 m. Such a rise may seem nominal but can have a significant impact in wetlands and other low-lying areas that potentially exchange nutrients and suspended sediments with the coastal ocean.

Coastal ocean waters range from quite cold (e.g., Gulf of Maine) to quite warm (e.g., Gulf of Mexico). Where large rivers enter coastal waters, such as the Mississippi River Plume and Chesapeake Bay Plume, visual discoloration can be observed because suspended material from land runoff and relatively high plankton concentrations contrast with the predominantly blue color of the open ocean. The Columbia River and the Mississippi River form an "estuary" mostly at sea, as very little of the diluted seawater is bounded by land.

Physical gradients are dynamic and change at multiple scales. Seasonal or wet and dry periods frequently differ depending on the various shelf gradients associated with estuarine, riverine, and ocean/shelf break processes. Regional geomorphology and physical mixing processes play a pivotal role in energy flow and material cycles. For example, the Loop Current in the eastern Gulf of Mexico may show seasonal reversals and vary seasonally in its penetration onto the shelf. Along-shore drift inside the north-flowing Gulf Stream off the Mid-Atlantic Bight tends to transport materials southward toward the North Carolina coast. Further south, the Gulf Stream forms a seaward boundary that tends to significantly isolate in-shore waters from those beyond the shelf break. Local current maps are available from the National Ocean Service of NOAA (www.noaa.gov; then click on nos).

Many different types of boundaries or fronts occur in coastal seas, but no formal classification exists. Alongi (1998) lists five categories:

- Shelf-sea (tidal) fronts
- Estuarine fronts or plumes
- Shelf-break fronts
- Upwelling fronts
- Island wakes and fronts caused by other land features

Fronts provide increased physical stability at local scales, which may positively influence primary production and energy flow to higher trophic levels (see Chapter 2).

Habitat/Community Differences

Presence of Mangrove/Seagrass and Coral Communities

Along the southeastern Florida Atlantic coast exists a combination of mangrove, seagrass, and coral reef ecosystems. In some localities, each community type may dominate the others, but often they co-occur. Seagrass communities may dominate certain shelf areas along the west coast of Florida (e.g., Big Bend region). The Flower Gardens, a disjunct coral community, exist off the southern coast of Texas. Alongi (1998) devotes chapters to coral reefs and mangrove ecosystems including factors regulating primary productivity (e.g., N and P). The role of N and P enrichment versus grazing in coral reef ecosystems is still strongly debated in the scientific literature (e.g., Miller et al. 1999). A paper by Chen and Twilley (1999) discusses soil nutrient relationships and productivity in a Florida Everglades mangrove ecosystem along an estuarine gradient (see the references cited above for the most recent perspective). These distinctive ecosystems provide a basis for local coastal waters classification. Mangrove communities also occur along the lower Texas coast, and seagrasses are a dominant community in Laguna Madre, TX.

Presence of Seaweed

Seaweeds are common algal communities in rocky intertidal zones (e.g., *Fucus* spp.), attaching themselves by means of a holdfast. Seaweeds belong to three marine algal classes: *Chlorophyceae* (green algae), *Rhodophyceae* (red algae), and *Phaeophyceae* (brown algae). The kelps (*Laminariales*), members of the brown algae, live subtidally but in relatively shallow waters and can form large forests along the cooler north Atlantic and Pacific coasts. These communities also may occur in the higher salinity reaches of estuaries. Alongi (1998) provides a discussion of primary production, factors limiting growth, nutrient cycling, and grazing in these communities.

CHAPTER 4

Variables and Measurement Methods To Assess and Monitor Estuarine/Marine Eutrophic Conditions

Causal and Response Variables
Field and Laboratory Methods
Nutrient Enrichment and Ammonia Toxicity

4.1 INTRODUCTION

This chapter provides an overview of several measurable trophic state variables that can be used to establish nutrient criteria for estuaries and nearshore coastal waters. Trophic state variables are those variables that can be used to evaluate or predict the trophic status or degree of nutrient enrichment of estuaries and nearshore coastal waters, especially when compared with reference conditions. The primary variables include two causal variables (TN and TP) and two response variables including a measure of algal biomass (e.g., chlorophyll *a* for phytoplankton or macroalgal biomass (AFDW) and water clarity, e.g., Secchi depth or electronic photometer), and the addition of dissolved oxygen, as appropriate. These variables are relevant at the national scale to practically all estuaries and are potentially relevant to nearshore coastal waters.

Several variables are important indicators of nutrient overenrichment for a large number of estuaries, but in many cases the data and supporting science are inadequate for most systems (e.g., algal species composition). Important secondary variables include seagrass and estuarine submerged aquatic vegetation (SAV) distribution and abundance, macroinfaunal community structure, phytoplankton species composition, and organic carbon concentrations, respectively. Seagrasses and SAV typically provide important shallow water habitat information, and hypoxia/anoxia are measures of loss of bottom habitat often associated with deeper waters. Organic carbon (total, particulate, and dissolved) is also included as a secondary variable because this variable is consistent with Nixon's (1995) definition of eutrophication. Changes in benthic macroinfaunal community structure often correlate with organic carbon enrichment and degree of hypoxia and anoxia (Diaz and Rosenberg 1995). The importance of algal species composition has implications for food webs (Roelke 2000). These variables are discussed in Chapter 2.

As indicated in Chapter 2, the concentration of the primary nutrient variables may not correlate well with one or more response variables in estuaries, especially hypoxia or anoxia and measures of phytoplankton biomass. In this case, predictive relationships should be attempted with nutrient loads using first empirical regression models or other statistical approaches if necessary to account for ecosystem-based nonlinearities. Application of mechanistic computer models is another approach (see Chapter 9).

Interpretation of nutrient enrichment indicators, especially for estuaries, is complicated by the interaction with measures of mixing and flushing as discussed in Chapters 2 and 3. Salinity gradients are associated with flushing but also play an important role in the type of biological communities exposed to nutrient enrichment. These physical considerations must always play a part in nutrient enrichment predictions including establishment of reference conditions as discussed in Chapters 2 and 6.

4.2 CAUSAL AND RESPONSE INDICATOR VARIABLES

Nutrients as Causal Variables

Nitrogen

Nitrogen is one of the most important limiting nutrients of autotrophic assemblages (e.g., phytoplankton and periphyton) incorporated into estuarine and nearshore coastal marine bioassessments. In those estuaries where N has been demonstrated to limit algal biomass production, it typically does so at higher salinities along the salinity gradient (Chapter 2). Most research has focused on the role of inorganic-N as a stimulant to algal biomass production (Stepanauskas et al. 1999). However, about 70% of the dissolved N transported by rivers worldwide (10^{12}g yr^{-1}) is dissolved organic N (DON) (Meybeck 1982). In contrast to P, control of N sources is more difficult because diffuse gaseous sources of N (N_2) can be assimilated directly from the atmosphere by N fixation, a process conducted by a variety of bacteria and cyanobacteria (blue-green algae). Also, dissolved inorganic N forms, especially nitrite and nitrate, are highly soluble and do not precipitate easily or sediment out when freshwater enters the brackish zone of estuaries as inorganic P is likely to do.

Total N measured as a water quality indicator consists of organic and inorganic forms. Although some dissolved organic N may be used for algal growth, especially if remineralized by bacterioplankton (Carlson and Graneli 1993; Seitzinger and Sanders 1999), it and particulate organic forms participate in algal biomass production through recycling processes (Chapter 2). In systems with hypoxic or anoxic conditions, the rate of decomposition is reduced. Although still an open question, apparently relatively little of the DON is directly utilized by phytoplankton, except for urea and free amino acids (Antia et al. 1991; Paerl et al. 1999). Dissolved organic N in rainwater (synthetic addition of urea and other constituents in bioassays) was shown experimentally to stimulate bacterioplankton and phytoplankton growth; however, the DON resulted in the dominance of diatoms and dinoflagellates whereas ammonium-N stimulated production more of small monads (Seitzinger and Sanders 1999). Further work is required to test whether this response is widely applicable. Thus, the source of DON can influence the degree of DON utilization by the microbial community. Inorganic N consists of ammonia, nitrite, and nitrate N. Ammonia N is a primary product of microbial degradation of organic N, and, if not used directly by autotrophic algae and vascular macrophytes and microbial heterotrophs for growth, it may be oxidized through nitrification to nitrite and nitrate. Varying proportions of organic N may be relatively refractive and contribute very little to N overenrichment problems. However, the readily recyclable component may contribute to N enrichment problems locally and further seaward. Some experimental or model analysis (e.g., box model) of the utilization of DON and in some cases particulate organic N for each coastal system is usually warranted.

In estuaries, N concentrations, especially the inorganic forms, typically vary widely seasonally, interannually, and along salinity gradients. In temperate river-dominated estuaries, nitrate concentrations may reach very high concentrations (e.g., >100 µM) in tidal fresh to brackish reaches (see Appendix G;

Neilson and Cronin 1981) due to wash-off associated with various land use activities including point and nonpoint sources (e.g., agricultural cropland). By late spring to early summer, the nitrate concentration may be below analytical detection limits. Nitrite concentrations seldom reach high levels in surface waters due to plant utilization and conversion to nitrate through nitrification. The principal bacteria genera that mediate nitrification include *Nitrosomonas*, but species of *Nitrosococcus*, *Nitrobacter*, and *Nitrospina* are also important (Sharma and Ahlert 1977, Watson et al. 1981). If dissolved oxygen is limiting nitrification, then nitrite may accumulate (Helder and de Vries 1983). Ammonia concentrations in open estuarine and nearshore coastal waters located away from point sources typically vary from below detection limits to approximately 1.0 to 5 µM, depending on growing season and rates of organic N decomposition. Much higher values may occur for relatively short periods. The ionized form of ammonia/ammonium is the most abundant reduced form and represents approximately 97% of the total (Sillen and Martell 1964). The equilibration between the ionized and un-ionized fractions is controlled by temperature, salinity, and pH, resulting in a range of un-ionized ammonia of 1% to 5% of the total at typical salinities, pH, and temperature (Emerson et al. 1975). Ammonia may be toxic to marine larvae, not just a stimulus to algal growth. Unionized ammonia concentrations in the range of 1.0µM approximate those that are known to be toxic to marine larvae, especially molluscs (U.S. EPA 1989). Denitrification may remove from a few to approximately 50% of the TN load entering temperate estuaries annually (Seitzinger 1988, Cornwell et al. 1999) depending largely on residence time of the water, sediment biogeochemical conditions (macroinfauna present to maintain irrigation, oxic conditions in the overlying bottom water), and water column depth. This process helps to modulate extreme DIN concentrations (Chapter 2). Typical values for dissolved inorganic N (DIN) and a few TN concentrations in estuaries and coastal nearshore waters are presented in Appendix G as a basis to help establish expectations for various coastal systems. It should be noted that N concentrations vary widely in space and time and the values in Appendix G are only intended to be rough guides. Specifics of analytical techniques to measure the various forms of N are included at the end of this chapter (Field Sampling and Laboratory Analytical Methods).

In open coastal waters of the North Atlantic Ocean at temperate latitudes, there is a typical seasonal progression in DIN and DIP concentrations associated with phytoplankton blooms. The spring bloom reduces these inorganic forms while phytoplankton biomass accumulates. This progression begins at lower latitudes and moves to higher latitudes. The spring bloom typically crashes in late spring, and summer biomass levels often are nutrient limited. Often a small bloom occurs in the fall following the fall thermocline breakdown that allows mixing and replenishment of nutrients from deeper waters into the upper surface layers, where a short burst of production occurs before light becomes limiting. Accumulation of deepwater nutrients during the winter has been used to assess the potential for spring-summer overenrichment in coastal seas based on trends in "salinity-nutrient mixing diagrams" (European Union Northern Marine Eutrophication Criteria Program, Ulrich Claussen, Germany, personal communication). Seasonal nutrient patterns in estuaries are quite variable. In some estuarine systems, a winter buildup of N and P has been observed (e.g., Patuxent River Estuary), especially when freshwater flows remained low and point sources dominated the nutrient supply (e.g., Flemer et al. 1970). Mixing diagrams also help interpret nutrient behavior in estuaries; however, some precautions are important to recognize (e.g., see Sharp et al. 1986).

At the interface between fresh and marine waters, a process occurs that results in an apparent increase in the ionized ammonia concentration. This process is apparently driven by the increased electrolyte solution of the salts, which has a significant impact on the production and nitrification process, thus yielding higher ionized ammonia levels (Rysgaard et al. 1999). Ionized ammonia adsorption to particles was decreased, especially in the 0 to 10% salinity range, as were the nitrification and denitrification processes. Further evaluation showed that the reduction in nitrification and denitrification processes was due not only to the displacement of bacteria and ionized ammonia from particles, but also to decreased bacterial activity. The projections from these studies were that ionized ammonia would be produced at a rate of 1 μM/g of sediment in the water. The changes in N dynamics that affect adsorption of suspended solids may need to be included when considering acceptable levels in fresh water sources to estuaries.

Phosphorus

Phosphorus is an important plant nutrient that may limit algal biomass production in tidal fresh to brackish zones of estuaries and some subtemperate to tropical marine coastal systems (Chapter 2). There are no common stable gaseous forms of phosphorus, so the phosphorus cycle is endogenic, without an atmospheric component (Manahan 1997). The main natural reservoirs of phosphorus are poorly soluble minerals (e.g., hydroxyapatite) in the geosphere. Erosion of these materials from terrestrial sources and their transport to the sea are important sources of new phosphorus in seawater. The phosphorus entering the sea is mostly orthophosphate, PO_4^{-3} (Kennish 1989). In previous decades, prior to widespread phosphate bans in detergents, estuaries received a considerable portion of P from detergents. The ban resulted for many estuarine systems in an elevated DIN:DIP ratio. In estuaries and nearshore coastal waters, phosphorus is present in dissolved inorganic form as well as dissolved and particulate organic form. Some fraction of P may be strongly embedded in a mineral matrix, and this renders that fraction relatively inert to biological utilization. For this reason, often measures of TP may represent some component that is not biologically available and managers should consider this in developing P criteria. Plants directly take up the phosphates as essential nutrients during photosynthesis. Some algae have the capability to break down dissolved organic P (DOP) with alkaline phosphatase (algal and free phosphatases) and utilize the phosphate as inorganic phosphate (Huang and Hong 1999). Alkaline phosphatase apparently is located on phytoplankton cell membranes, which makes it difficult to determine whether the uptake is direct for DOP or the DOP undergoes enzymatic hydrolysis on the cell membrane. Malone et al. (1996) suggested by inference that Chesapeake Bay phytoplankton may utilize organic sources of P, in part, because the DIN:DIP thresholds approach 160, which is considerably greater than the N:P ratio reported by Redfield et al. (1963). Orthophosphates are typically preferred by autotrophic phytoplankton, although some assimilation of organic phosphorus may occur, especially during periods of P deficiencies (Boney 1975). When plants die, or are eaten, the organic phosphorus is rapidly converted to orthophosphates through the action of phosphorylases within fecal material, phosphatases in the plant cells, and finally by bacteria (Riley and Chester 1971).

To summarize, phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates, and organically bound phosphates (common analytes are total phosphorus [TP] and dissolved or particulate organic phosphorus [DOP, POP]). These compounds may be soluble, in particulates or detritus, or incorporated as organic P in organisms. Phosphorus is essential to the growth of organisms and can limit phytoplankton biomass production, which is most commonly observed in freshwater systems (Hecky and Kilham 1988) and some estuaries and coastal marine systems (Chapter 2). In instances where phosphate is limiting, the discharge of raw or untreated wastewater, agricultural drainage, or certain industrial wastes may stimulate the growth of algae. Appendix G provides examples of P concentrations in several forms.

Silica

Silica, as an important algal nutrient, has received much less attention in estuarine nutrient overenrichment studies than N and P based on the limited volume of literature citations (e.g., see Malone et al. 1996) and recent reviews of estuarine eutrophication (Chapter 1). Silica limitation of diatom production, a major algal group that requires Si (and silicoflagellates), often is a measure of N or P overenrichment (D'Elia et al. 1983; Conley and Malone 1992). Dissolved Si is a product of weathering and erosion of rocks on land with subsequent transport to the sea (Conley and Malone 1992). Because Si has essentially no human sources, except possibly from erodible soils under human influence, it is not a strong candidate for regulation. In some parts of the ocean, organisms (such as diatoms and radiolarians) abound that have produced skeletons of a noncrystalline form of hydrated silica-opal. As these skeletons settle to the sea floor they slowly dissolve, releasing silica. Officer and Ryther (1980) predicted that increases in N and P to estuaries and coastal waters from human activities, coupled with the reduction in silicates to the sea from construction of artificial lakes, would alter the N:Si and P:Si ratios. These alterations were postulated to alter phytoplankton populations to reduce the relative abundance of diatoms and enhance the relative abundance of flagellates. Egge and Aksnes (1992) showed that diatoms always numerically dominated the phytoplankton community when concentrations of silica were in excess of 2.2 µM. Dominance by diatoms ceased or became more variable when concentrations of Si were less than this value.

Ryther and Officer (1981) reinterpreted the relationship of N pollution in Long Island Inlets during the 1950s. Nitrogen may have limited the nuisance *Nannochloris,* blooms but they hypothesized that the bloom persisted because diatoms had been eliminated by Si depletion. Also, the degree of Si limitation of spring diatom blooms in Chesapeake Bay that fuel summer anoxia has direct ecological implications (Conley and Malone 1992, Malone et al. 1996). Freshwater sources of Si dominate estuarine supplies (Fisher et al. 1988). Typically, Si limitation can be potentially deduced from ambient ratios relative to the nutrient-sufficient N:Si:P biomass ratios of 16:16:1 (Redfield et al. 1963; Conley et al. 1993). In Chesapeake Bay, the dissolved Si:DIP ratio often approximates 100-300 (Malone et al. 1996), suggesting strong Si limitation. Significant increases in Mississippi River N and P concentrations and loading and decreases in silicate have occurred during the 20th century (Rabalais et al. 1996). The increased P loading and associated increased diatom production and eventual burial in river sediments, as predicted by Officer and Ryther (1980), has resulted in a reduced Si supply to the coastal environment. The consequence is that diatom production, generallly a preferred phytoplankton group to support higher trophic levels, is now more Si limited than in previous decades. The N:P:Si ratios on coastal Louisiana and Texas now suggest the possibility of a joint nutrient limitation of phytoplankton production.

Silica concentrations for the Coastal Texas/Louisiana coast averaged approximately 5.3 µM in the late 1980s but averaged about 9.0 µM during the early 1960s. Silicate concentrations in the Chesapeake and Delaware Bays and the Hudson River Estuary ranged from about 90 to near detection levels, 30 to near detection limits, and 30 to 3 µM, respectively (Fisher et al. 1988). Eyre and Balls (1999) reported that Si was less likely to limit diatom production in tropical estuaries than in temperate ones because concentrations tend to be much higher in tropical estuaries.

The role of silica may be more important to diatom species composition and food quality as future research may document. More attention in the future should be given to the measurement and assessment of the role of Si in estuarine and nearshore coastal primary productivity and food web dynamics and as a basis for controlling co-limiting N and/or P.

Response Variables

Chlorophyll a and Macroalgal Biomass

Chlorophyll *a* is the molecule mediating photosynthesis in most all green plants (except prochlorophytes, which contain divinyl chlorophyll), including phytoplankton; it is relatively easy to measure either spectrophotometrically or by fluorescence and is commonly used to indicate phytoplankton biomass. However, the amount of chlorophyll per cell can vary widely. Conversion factors from weight of chlorophyll to weight of carbon (a desired biomass unit) can vary by a factor of 10. Adaptation to light levels is the primary reason for observed variability; photoadaptation can cause the chlorophyll per cell to vary widely. The technology for measuring chlorophyll has greatly improved over the decades. The Welschmeyer (1994) fluorometric analysis reduces the interference due to chlorophyll *b* and phaeopigments. The HPLC procedure is capable of detecting and quantifying various pigments characteristic of different algal groups (e.g., diatoms, cyanophyta, chlorophyta, and dinoflagellates) (Jeffery et al. 1997).

Rapid proliferation or blooming of phytoplankton, as reflected in chlorophyll *a* measurements, occurs throughout the ocean but is most often associated with temperate coastal and estuarine waters and at higher latitudes. In winter months, growth of phytoplankton populations is generally minimal because of insufficient light and also because a turbulent and unstable upper water column carries the phytoplankton cells below the euphotic zone (where light is not sufficient) before they can divide.

Chlorophyll *a* concentrations vary widely as a function of nutrient supply, water column stability, euphotic zone depth (light availability), sinking, grazing, disease organisms (e.g., viruses), and flushing/mixing (Chapter 2). Values in excess of 12 to 15 µg/L are likely to cause severe shading of seagrasses (Kelley in press). Concentrations in estuaries during summer optimum growing conditions may exceed 50 to 80 µg/L when nutrient loading is high (Monbet 1992). Summer values in the range of 20 to 40 µg/L are frequently observed in enriched estuaries. In contrast, concentrations in overenriched temperate U.S. estuaries during the winter may decrease to 1 to 5 µg/L Nearshore coastal areas removed from high nutrient loads may experience chlorophyll concentrations in the range of approximately 1 to 3 µg/L (Appendix G). Very high values may occur during the summer under conditions of high levels of nutrient enrichment (e.g., the Mississippi River Plume on the Texas/Louisiana Shelf [Rabalais et al. 1996]).

Macroalgal biomass, especially benthic unattached forms (i.e., *Ulva* spp.), often becomes abundant in relatively shallow estuaries that experience nutrient overenrichment. In estuaries that receive most of their nutrient load from groundwater (e.g., Waquoit Bay, Cape Cod, MA; see Chapter 2) benthic macroalgae may shade out seagrasses. Continued enrichment typically leads to reduction of macroalgae as phytoplankton predominate in the water column. Macroalgae are difficult to adequately sample for chlorophyll *a,* and thick mats often contain sheets of algal material that has begun to degrade. The most common method to sample benthic macroalgae is to collect samples and express the biomass on a dry weight basis.

Measures of Water Clarity

Light Attenuation Coefficient

The Secchi disc has been a mainstay as a tool in estimating water clarity; however, this simple and inexpensive tool does not provide all of the information required to distinguish the light attenuation effects of living phytoplankton pigments (i.e., traditionally estimated by chlorophyll *a*) from other factors (e.g., inorganic suspended sediments, organic nonchlorophyll-based detritus, and humic-like materials) that reduce water clarity. EPA's Chesapeake Bay Program (Chapter 2) has developed an analytical approach that partitions the effect of chlorophyll *a* from total suspended solids that contribute to reduction in water clarity. This approach has been used successfully in estimating the combined factor contribution to light attenuation over submerged aquatic vegetation beds (Dennison et al. 1993). In turbid coastal waters, the analyst should be aware of lower values for the constant 1.7 to estimate the light attenuation coefficient (see Giesen et al. 1990 and references in Chapter 2). More precise estimates of the light attenuation coefficient can be made with electronic submersible light meters including PAR meters (photosynthetic active radiation) and submersible spectral radiometers. These meters are now in widespread use, and their use should be encouraged because they give a direct measure of light attenuation, especially in shallow water where depth may limit use of the Secchi disc.

Attenuation of light in the sea in nonalgal bloom areas is determined principally by the amount of suspended matter present, but in estuaries and nearshore coastal waters, color from humic-like materials may significantly compete with particulate material in light attenuation. In moderately turbid coastal waters, 1% of the surface visible light energy may penetrate to a depth of only 10 to 20 m, but in shallow estuaries depths often are from 10 cm to 3 m or so. There typically is a strong seasonal variability in water clarity in temperate estuaries between the active growing season and the winter, and in subtemperate to tropical estuaries water clarity often is a function of the wet season. In the Atlantic temperate open coastal areas with the coming of spring, the depth of the euphotic zone often increases and the depth of the mixed layer decreases because of the development of the seasonal thermocline. This allows a spring bloom to develop. The thermocline tends to confine the algal cells to the euphotic zone, which becomes rich with nutrients as a result of winter mixing. In estuaries, the pycnocline may also have this effect. In partially mixed estuaries where light is adequate at depth, diatoms may grow below the pycnocline (Malone et al. 1996). If the necessary growth-promoting factors are also present, conditions are optimal for proliferation of phytoplankton from seed stock, which may be either the plankton cells themselves or their resting stages (Riley and Chester 1971).

Secchi Depth

The Secchi disc is a useful tool to estimate water clarity (Holmes 1970). Secchi disc measurements often have a longer historical record than electronic measurements, which facilitates assessment of trends in water clarity. Secchi depth measurements are obtained with a 40 cm plastic or metal Secchi disk that is either white or is divided into black and white quadrants on a nonstretchable line that is calibrated in decimeters. The disc should be weighted to maintain a level position, especially under strong current conditions. The disk is lowered into the water until it disappears from view and the depth is recorded. The disk is then slowly raised to the point where it reappears and the depth is recorded again. The mean of these two measurements is the Secchi depth. Observations are made from the shady side of the vessel to reduce problems of glare; however, when a small boat is used for field work a "viewing tube" allows readings under full sunlight conditions. Measurement should be made without sunglasses.

Dissolved Oxygen

Dissolved oxygen (DO) is an integrative measure of ecosystem health and habitat function. As a first-order estimate, the percent saturation of surface and bottom waters is an index of the production/respiration ratio. Dissolved oxygen in bottom waters serves as a measure of habitat availability for benthic animals and pelagic animals that feed on the bottom. EPA has developed saltwater DO criteria for coastal waters between Cape Cod and Cape Hatteras (see www.epa.gov/ost/standards/dissolved). Profiles of DO are indicative of oxygen depletion conditions such as hypoxia and anoxia. Lack of oxygen in bottom waters causes sediment to release dissolved nutrients including orthophosphorus, ammonia, and in addition, toxic hydrogen sulfide.

Carbon Compounds

Organic matter content is typically measured as total organic carbon (TOC) and dissolved organic carbon and is an essential component of the carbon cycle. The rate of organic carbon production and decomposition and the resulting microbial biomass are at the heart of the eutrophication problem. Evaluation of the carbon-containing compounds in an aquatic ecosystem can indicate its organic character. The larger the carbon or organic content, the greater the growth of microorganisms that can contribute to the depletion of oxygen supplies. TOC is a more convenient and direct expression of organic carbon content than are the biochemical oxygen demand (BOD), assimilable organic carbon (AOC), or chemical oxygen demand (COD) methods. TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements, such as N and hydrogen, or inorganics that can contribute to the oxygen demand measured by BOD and COD. In spite of its versatility, TOC does not provide the same kind of information as BOD, AOC, or COD, and should not be used to replace these methods.

At the surface of the sea, the concentrations of particulate and dissolved organic carbon range up to 12.5 μM and between 75 and 150 μM, respectively. In coastal environments, concentrations of dissolved and particulate organic carbon are greater by factors of ~7-fold. Concentrations of dissolved and particulate organic carbon in surface waters are equivalent to 150 to 1,800 µg C/L (Millero 1996). Organic carbon represents approximately 50% of the dissolved and particulate organic material in seawater (Millero 1996). However, the major form of carbon in seawater is associated with inorganic carbonate systems.

Benthic Macroinfauna

Benthic macroinfauna are an important biological component of estuarine and nearshore coastal marine ecosystems. These communities contribute to benthic food webs, contribute to nutrient cycling and system productivity through benthic-pelagic coupling of nutrient recycling, help stabilize bottom habitats, and contribute to marine biodiversity. Benthic infaunal communities are quite diverse within an estuary or coastal region. Diversity is a function of salinity, with higher diversities associated with higher salinities (Carriker 1967). Sediment irrigation provided by benthic infauna enhances denitrification by increasing the flux of ammonium into oxic microenvironments where nitrification can occur and the flux of nitrite and nitrate into the anoxic sediment zone where denitrification becomes possible (Chapter 2).

4.3 FIELD SAMPLING AND LABORATORY ANALYTICAL METHODS

The following sections provide additional information on field sampling and laboratory methods for selected variables. A list of suggested methodologies for analysis of biochemical parameters is provided in Table 4-1. These methods have been summarized from nationally or regionally recognized reference compendiums (APHA 1998, ASTM 1976, U.S. EPA 1979, Spotte 1992) and provide acceptable methods for determining the concentrations of nutrients as well as acceptable methods for measuring the effects of those nutrients in estuarine and marine waters.

Field Sampling Methods

Nutrients, Hydrography, and Sediments

Physiochemical profiles should be recorded for each field sampling station. Important parameters to be measured include water temperature, pH, dissolved oxygen, salinity, light attenuation, surface radiation, and total depth. Generally, a multiparameter water quality instrument CTD is used. Sampling depth will vary depending on specific objectives; however, enough vertical depth reading should be taken to characterize the physical structure of the water column. For example, CDT measurements might be taken at frequent intervals in the vicinity of the pycnocline (e.g., every 0.1 m in highly stratified estuaries). Overall current dynamics can be mapped with oceanographic tools such as current meters, drift cards, and acoustic Doppler sounders.

Field sampling of discrete water samples for laboratory analysis can be performed using standard nonmetallic plastic water bottles. Samples are drawn into prelabeled bottles and fixatives are applied as appropriate to the subsequent analysis. Nutrient and organics samples are stored on ice until reaching a shoreside sample handling location. Nutrient samples are filtered using graduated syringes and then frozen. Samples for total TN and TP are filtered or unfiltered as appropriate, and 20 mL of sample is frozen for analysis. See Chapter 5 for additional sampling protocols.

Table 4-1. Suggested methods for analyses and monitoring of eutrophic conditions of coastal and marine environments (* = primary EPA preferred causal and response variables)

Eutrophication indicators	Suggested methods	Detection limit or range	Comments	References
Field				
*Water clarity	Secchi depth	0.1 m	—	EPA 903-R-96-006
pH	CTD probe	0.01 pH	—	—
Dissolved oxygen	CTD probe	0.02 mg DO/L	or Winkller Azide Mod.	—
Salinity	Salinometer	0.1 psu	—	—
Light attenuation	Sensor	0.05%@100%light	e.g., LI-COR-LI-192S A sensor	—
Temperature	CTD probe	0.1°C	—	—
Laboratory analyses				
*Total phosphorus	SM 4500P-E	0.3 µM	Ascorbic acid method	APHA 1998
(including orthophosphate,	SM 4500P-E	0.32 µM	Auto. persulfate method	APHA 1998
POP,, and DOP)	EPA 365.2	—	—	EPA 600/4-79-020
	CBP IV.D.2	0.03 µM	Auto. persulfate method	EPA 903-R-96-006
Dissolved orthophosphate	CBP IV.D.3	0.02 µM	Ascorbic acid method	EPA 903-R-96-006
Particulate phosphorus	CBP IV.D.4	0.04 µM	Ascorbic acid method	EPA 903-R-96-006
*Total N, incl. DON,	SM 4500N-C	0.36 µM	Persulfate method	APHA 1998
DIN, and PON[a]	ASTM D3867	0.7-143 µM	Persulfate method	ASTM 1976
	EPA	—	Persulfate method	EPA 903-R-96-006
	EPA-AERP18	—	—	EPA 600/4-87-026
	CBP IV.D.8	1.9 µM	Auto. persulfate method	EPA 903-R-96-006
Total Kjeldahl N	SM 4500org-C with	—	Semi-micro-Kjeldahl method	APHA 1998
	SM 4500NH3-H	1.4-1429 µM	Auto. phenate method	APHA 1998
	EPA 351.3/.1 (mod.)	—	Colorimetric/titration	EPA 600/4-79-020
Ammonia/ammonium	SM 4500NH3-B/H	1.4-1429 µM	Auto. phenate method	APHA 1998
	EPA 350.1	0.7-1429 µM	Colorimetric phenate	EPA 600/4-79-020
	CBP IV.D.7	0.3 µM	Auto. phenate method	EPA 903-R-96-006
Nitrate	SM 4500NO3-F	35.7-714 µM	Auto. cadmium reduction	APHA 1998
	EPA 353.2	—	—	EPA 600/4-79-020
Nitrite	SM 4500NO3-F	35.7-714 µM	Auto. cadmium reduction	APHA 1998
	EPA 353.2	—	—	EPA 600/4-79-020
	SM 4500NO2-B	0.7-71 35.7-714 µM	Colorimetric method	APHA 1998
	EPA 354.1	—	—	EPA 600/4-79-020

Table 4-1. Suggested methods for analyses and monitoring of eutrophic conditions of coastal and marine environments (* = primary EPA preferred causal and response variables) (continued)

Eutrophication indicators	Suggested methods	Detection limit or range	Comments	References
	CBP IV.D.5	0.01 μM	Auto. colorimetric method	EPA 903-R-96-006
Nitrate + nitrite	SM 4500NO3-F	35.7-714 μM	Auto. cadmium reduction	APHA 1998
	EPA 353.2	—	—	EPA 600/4-79-020
	EPA 4.1.4	0.7-143 μM	Technicon autoanalyzer	EPA 503/2-89/001
	CBP IV.D.6	0.01 μM	Auto. colorimetric method	EPA 903-R-96-006
Particulate N	CBP IV.D.8.10	1.36 μM	Filtration/combustion	EPA 903-R-96-006
Total organic carbon	SM 5310TOC-D	>0.1 mg C/L	Wet oxidation method	APHA 1998
	SM 5310TOC-C	>0.01 mg TOC/L	Persulfate method	APHA 1998
	EPA 415.1	—	—	EPA 600/4-79-020
Dissolved organic carbon	SM 5310TOC-C	>0.01 mg TOC/L	Persulfate method	APHA,1998
	EPA 415.1	—	—	EPA 600/4-79-020
	ASTM D2574-79	—	—	ASTM 1976
	CBP IV.D.10	0.5 mg/L	Catalytic combustion	EPA 903-R-96-006
Particulate carbon	CBP.IV.D.9	0.097 mg/L	Filtration/combustion	EPA 903-R-96-006
Total silicates	SM 4500SiO2-D	0.33-0.83 μM	Heteropoly blue method	APHA 1998
	ASTM D859-68	—	—	ASTM 1976
	CBP-IV-15	0.17-23.3 μM		EPA 903-R-96-006
	EPA 370.1	—	—	EPA 600/4-79-020
	CBP IV.D.15	0.22 μM	Molybdosilicate method	EPA 903-R-96-006
Total suspended solids	SM 2540-D	2-20,000 mg/L	Dried at 103-105°C	APHA 1998
	CBC IV.D.13	2.0 mg/L	Filtration/heat	EPA 903-R-96-006
Total volatile solids	SM 2540-E	—	—	APHA 1998
	Estuarine	—	—	EPA 430/9-86-004
BOD	SM 5210-B	—	5-day method	APHA 1998
	EPA 405.1	—	—	EPA 600/4-79-020
	CBP IV.D.11	—	5-day method	EPA 903-R-96-006
COD	SM 5220-D	—	—	APHA 1998
	EPA 410.4	—	—	EPA 600/4-79-020
Biological measures				
Phytoplankton biomass	—	—	—	—
Zooplankton biomass				
Chlorophyll *a*[b]	SM 10200-H	0.01 mg/M^3	Fluorometric, HPLC, Spectro.	APHA 1998

Table 4-1. Suggested methods for analyses and monitoring of eutrophic conditions of coastal and marine environments (* = primary EPA preferred causal and response variables) (continued)

Eutrophication indicators	Suggested methods	Detection limit or range	Comments	References
	EPA AERP12	—	—	EPA 600/4-87-026
	ASTM D3731-79		Spectrophotometer	ASTM 1976
	CBP IV.D.12	1.0 µg/L	Spectrophotometer	EPA 903-R-96-006
Phaeophytin	SM 10200-H	0.01 mg/M^3	Fluorometric, HPLC, Spectro.	APHA 1998
	EPA AERP12	—	—	EPA 600/4-87-026
	ASTM D3731-79	—	Spectrophotometer	ASTM 1976
	CBP IV.D.12	1.0 µg/L	Spectrophotometer	EPA 903-R-96-006
Dinoflagellate density	—	—	—	—
Diatom density	—	—	—	—
Dinoflagellate/diatom	—	—	—	—
Perennial plant density	—	—	—	—
Ephemeral plant density	—	—	—	—
Epiphytic growth	—	—	—	—
Phytoplankton blooms	—	—	—	—
Fish kills	—	—	—	—

[a] DON, dissolved organic N, DIN, dissolved inorganic N; PON, particulate organic N.

[b] Phytoplankton segments: The HPLC procedure is capable of detecting and quantifying various pigments characteristic of different algal groups (e.g., diatoms, cyanophyta, chlorophyta, and dimoflagellates) (Jefferey et al. 1997).

Laboratory Analytical Methods

Detailed methods and references are given in Table 4-1. Some general considerations are presented in the following sections.

Water Column Nutrients

Nitrogen Compounds

Several methods have been used to determine the concentration of N species in the marine environment. Methods presented in this document are relatively easy to use, do not require extensive instrumentation, provide detection limits below those expected in marine environments, and are in general use by many investigators. The most common forms of N in eutrophication evaluation in order of decreasing oxidation state are nitrate, nitrite, ammonia, and organic N. The sum of these is expressed as TN and is not to be confused with total Kjeldahl N (TKN), which is the sum of organic N and ammonia. Total N can be determined through oxidative digestion of all digestible N forms to nitrate, followed by quantitation of the nitrate. Nitrite is an intermediate oxidation state of N, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Such oxidation and reduction may occur in wastewater treatment plants, water distribution systems, or natural waters. Ammonia is produced largely by deamination of organic N-containing compounds and by hydrolysis of urea. The two major factors that influence selection of the method to determine ammonia are concentration and presence/absence of interferences (e.g., high concentrations of colored organic substances such as humic-like materials or paper mill effluents).

Total N is measured by the persulfate method, which digests all organic and inorganic – containing compounds. All N-containing materials (except nitrogen gas) are measured after sample digestion has occurred. Various organizations have adjusted sample volume or automated the process and produced different ranges of detection. The lowest detectable concentration is ~ 0.7 µM of TN. This is in the range of the measured available N (0.7 to 5.0 µM TN) for studies performed off the continental shelf in the North Atlantic from 1956 to 1958 (Kennish 1989). Kjeldahl N minus the ammonia concentration is the surrogate measurement for all organic N-containing compounds.

Ammonia/ammonium is measured by the indophenol blue (= phenate) or specific ion electrode methods after conversion of ammonia and ammonium to ammonia. This is done by raising the pH of the sample above 11. This method has some essential features (e.g., minimal interference from waters highly stained with humic materials and paper mill effluents); however, the level of detection is relatively high (e.g., 2.0 µM NH_3-N) but adequate for ammonia-rich waters (Flemer et al. 1998). Ammonia electrodes do not work directly in seawater. In the spectrophotometric methods, the ammonia is reduced to monochloramine and then reacted with phenol to form a blue color. In the specific ion electrode method, the ammonium is converted to ammonia using a strong basic solution and partial pressure of ammonia gas (i.e., free ammonia) in solution, which is related to the dissolved ammonia concentrations by Henry's Law.

Nitrates and nitrites are measured in combination using the cadmium reduction procedure of Wood et al. (1967). This colorimetric method determines the concentration of these two materials after reaction of nitrites to produce an azo dye, the color of which is proportional to the concentration of the combined nitrates and nitrites. Total nitrate is determined by subtracting the concentration of nitrite from the combination of the two. The process for measurement of nitrite produces the same azo dye as the combined measure, but without the Cd reduction. The difference in these two measures is the nitrate concentration.

Phosphorus

The target detection limit for measurement of P in seawater is ~ 0.3 µM. The procedures for the measurement of total particulate and dissolved P as well as orthophosphate in seawater provide detection limits that are less than this value (U.S. EPA 1996). These procedures convert the phosphorus-containing compounds to orthophosphate through the digestion of the sample with alkaline persulfate. This treatment is then reacted with ammonium molybdate and antimony potassium tartrate in acidic solution to produce an intense blue complex with ascorbic acid. Interferences with elevated concentrations of Si can be avoided by maintaining an acid concentration in the reagents and analyzing the material at elevated temperatures of ~37°C. The resulting phosphomolybdic acid reduction produces a purple-blue complex that is measured at 885 nm on a spectrophotometer. This method of measuring reactive silicate is recommended in Millero (1996).

Silica

The target detection limit for measurement of Si in seawater is ~0.7 µM. Producing pigmented silicomolybdate complex by procedures contained in U.S. EPA (1996) provides adequate sensitivity after the samples are filtered (0.45 µm GF/F filter) to remove interfering particles and turbidity, and after the interferences of phosphates and arsenates are removed with oxalic acid. The resultant filtrate is treated with a solution containing metol-sulfate (p-methyl-amino-phenol sulfate) to produce a blue color that is evaluated more efficiently than the yellow color recommended for evaluation in U.S. EPA (1996), with a spectrophotometer at 812 nm (Strickland and Parsons 1968). This method of measuring reactive silicate is also recommended in Millero (1996).

Carbon

Total carbon consists of inorganic and organic forms that are in particulate and dissolved size classes. The distinction between total and organic carbon is based on acidifying samples to remove the inorganic forms and filtering through 0.45 µm GF/F filters to remove the particulate forms. Total carbon is measured by burning the sample to release the particles contained on the glass fiber filter. This converts the carbon to CO_2, which is then transported to a thermal conductivity detector for measurement. The carbon left behind in the filtrate is catalytically combusted using a platinum catalyst at ~680°C that is then transported to a nondispersive infrared detector. The EPA methods (U.S. EPA 1996) will provide adequate detection of both dissolved and particulate carbon in the total and organic phases. The difference in total carbon and organic carbon represents the inorganic fractions that are primarily $CaCO_3$ shells.

Sediment Analyses

Bulk Sediment

Cores are collected from field sites to help determine the historical record and sedimentation rate. Short cores, the upper 30 cm of the substrate, can be obtained with a HAPPS core, designed to collect a relatively undisturbed core of surficial sediment (Kannerworff and Nicolaisen 1973) and used to profile sedimentary particulate organic carbon and N. Carbon-N analyses follow the method of Hedges and Stern (1984); samples for dissolved constituents in pore water are extracted either by whole-core squeezing or by centrifugation (Devol et al. 1997, Brandes and Devol 1995, Lambourn et al. 1991). Deep coring devices are used to collect continuous sediment core samples 2 to 3 m into the sediment bed. These deeper cores are used for analysis of ^{210}Pb, carbon and N, sulfide, and biogenic silica in order to determine burial rates of ^{210}Pb and ^{210}Ra.

The sedimentation rate is estimated based on the change in activity of naturally occurring ^{210}Pb radionuclide produced at a constant rate from the decay of ^{210}Ra, using the excess ^{210}Pb inventory method of Anderson et al. (1987). Excess ^{210}Pb is determined from the difference between total ^{210}Pb activity in the sediment and the activity of the background ^{210}Pb being produced from ^{210}Ra. To collect samples for measurement of ^{210}Pb and ^{210}Ra activity at depth with the sediment, cores are sectioned and each section is then homogenized and placed in a precleaned 16 oz jar, with a small subsample removed and placed into a glass vial for particulate C and N analysis (Evans-Hamilton, Inc. 1998).

The excess ^{210}Pb inventory method yields accumulation rates (g/(cm^2/yr)), which are converted to a sedimentation rate (cm/yr) using the bulk sediment density g/cm^3. For evaluation of seasonal trends, the upper cm is subsampled at 0.25 cm intervals, and in 1 cm intervals below the first cm, following the assumption that any seasonal storage of N or carbon would manifest almost entirely at the surface of the sediment.

Pore Water Profiles

Pore water profiles of manganese, iron, nitrate, and oxygen demonstrate that oxidation of iron and magnesium yields less energy than does oxidation of carbon by oxygen or nitrate. Consequently, concentration peaks of these species are located below the depletion depths of oxygen and nitrate. In anaerobic environments, after the supplies of oxygen, nitrate, manganese, and iron are exhausted, sulfate reduction is the dominant mode of organic matter oxidation and nutrient remineralization.

Sulfate reduction rate can be measured with the radiotracer method of Christensen et al. (1987). A significant fraction of the oxygen flux may be consumed by the reoxidation of sulfide produced during sulfate reduction (Canfield 1993).

Sediment traps are used to measure the quantity and composition of the flux of materials settling through the water column to the sediment. There are four materials of interest: chlorophyll as an indicator of planktonic algal remains, pheaopigments as an indicator of degraded plankton that has been consumed by zooplankton, particulate organic carbon (POC), and particulate organic N (PON). Total sedimentation rate is corrected for resuspension materials in order to derive the net flux to sediment. Samples are collected by in situ benthic flux chambers, and measurements of oxygen, silicate, nitrate, ammonium, phosphate, and N gas are made (Evans-Hamilton, Inc. 1998).

Determination of Primary Productivity

Primary productivity refers to the growth rate of the phytoplankton community and is commonly measured using trace amounts of radioactive carbon (as bicarbonate) that label the photosynthetic reaction. Additional variables are measured to support these data: biomass (as estimated by chlorophyll *a*), incoming solar radiation, and nutrient concentrations at depth. Primary productivity, P, is defined as

$$P = \mu \times B$$

where μ is the specific growth rate (growth normalized per cell) and B is the biomass of the phytoplankton population (amount of cells). These variables are > 'compound' = as they in turn depend on other variables. Growth rate depends on light (solar radiation), dissolved nutrients in the water column, and water temperature. The phytoplankton biomass is determined by the net result of growth and loss (grazing, mixing, sinking) processes and reflects enrichment conditions.

To estimate primary productivity, samples are collected at varying depths corresponding to predetermined light levels. Fresh samples at each light level are collected for analysis of chlorophyll *a*, nutrients, and primary productivity in two sets of two clear bottles and one dark bottle; each set is filled for ambient treatment and nutrient spike treatment. Nutrient spiking consists of adding an initial concentration of 10 μM N (NH_4CL) and 1 μM phosphorus (KH_2PO_4) to seawater. Nutrients are monitored from additional samples collected and tested for nitrate, nitrite, ammonium, orthophosphate, and silicate. Samples are inoculated with ^{14}C-labeled sodium bicarbonate and, if appropriate, the nutrient spike, and placed in a screened bag to simulate the light level from which they were collected. Samples are incubated at in situ conditions for 24 hours and then transported to the laboratory for filtration using glass fiber filter paper (Whatman GF/F, nominal pore size 0.7 μm or smaller pore size). The filters are placed into vials containing EcoLume scintillation cocktail. The specific activity of the filtered particulates is measured in a scintillation counter. Primary production is calculated as mg C/(m^3/day) using the basic equations found in Parsons et al. (1984) (Evans-Hamilton, Inc. 1998).

In productive coastal waters, measurements using the light and dark bottle technique with changes in dissolved oxygen often can be used in place of the ^{14}C method (Strickland and Parsons 1968). In some cases, free water gas-based (e.g., DO) methods are possible to measure ecosystem metabolism (Odum 1956; Odum et al. 1959; Kemp and Boynton 1980).

Phytoplankton Species Composition

Samples collected from the field are analyzed to identify and enumerate autotrophic phytoplankton, as well as heterotrophic dinoflagellates and microzooplankton species. From 20 to 50 mL aliquots of samples are settled in separable counting chambers for at least 24 hours before examination under phase-contrast optics with an inverted microscope following the classic Utermöhl technique (Lund et al. 1958). A single transect across the center of the chamber is counted at 390× magnification for flagellates; 150× magnification is used for other organisms. From 25% to 100% of the chamber bottom is examined, depending on cell concentrations in the sample. Appropriate multipliers are used to convert all counts to common units of cells/L (Sournia 1978). Organisms are identified to the lowest taxonomic category possible. Even quite small changes in the physical and chemical parameters and availability of micronutrients can have a significant effect on the growth constants of algae. A difference in doubling time of 25% between two fast-growing organisms can lead to one outnumbering the other by 15 to 1 in a week and quickly lead to alterations in species assemblages (Riley and Chester 1971).

There are numerous algal species in estuarine and open coastal waters that are considered to be harmful (e.g., see Dortch et al. 1998, Anderson and Garrison 1997, Anderson 2000). This is a rapidly changing area of marine ecology and experts should be consulted for specific taxonomic identifications.

Macrobenthos, Macroalgae, and Seagrasses and SAV

Macroinfauna are typically sampled with coring devices or bottom grab samplers and wet-sieved through 0.5 μM mesh sieves to separate the animals from very fine sediments. Stacked sieves can be used to remove larger shell fragments and sand particles. A relaxant (e.g., 0.3% propylene phenoxytol) is applied prior to addition of formalin. Samples are usually preserved in 10% buffered formalin for several weeks and then transferred to 60%-70% isopropanol (Diaz and Rosenberg 1995).

Macroalgae are typically sampled by collecting algal material by hand from a known surface area of the habitat. Various devices may be used (e.g., 0.5 m stainless or plastic hoop).

Both above- and below-ground seagrass and SAV biomass can be collected from a known area of the bed. Various techniques have been used. An often-used method is to shove metal strips along the sediment surface in a square meter pattern and anchor the strips at all four corners by pushing a sharp spike through holes drilled at each end of the strips. Then, the plant material separated to species can be clear-cut with sharp shears and taken to the laboratory and dried in a heated cabinet at 60°C to constant dry weight. A sharp spade is required to collect below-ground roots and rhizomes. This material should be identified and dried to constant weight.

CHAPTER 9

Use of Models in Nutrient Criteria Development

All models are wrong. Some models are useful.
(George E. P. Box)

9.1 INTRODUCTION

This chapter addresses the role of models in nutrient criteria development. It is closely linked to Chapter 5, which addresses database development, sampling designs, and monitoring. One system is said to model another when the observable variables in the first system vary in the same fashion as the observable variables in the second (NRC 2000). Chapter 7 of the NRC report goes on to state that models come in many forms. They may be empirically derived statistical relationships plotted on a graph, physical analogues (e.g., mesocosms) of the system of interest, analogues of different systems that have useful parallel relationships of observable factors (e.g., from physics, the flow of water through pipes to model the flow of electrons through an electrical circuit), or numerical models run on computers that are based on first principles or empirical relationships.

Environmental water quality models have several uses (e.g., reduce ecosystem complexity to a manageable level, improve the scientific basis for development of theory, provide a framework to make and test predictions, increase understanding of cause-and-effect relationships, and improve assessment of factor interaction). Reliable predictions stand out as a salient requirement because of the social and economic consequences if predictions are unreliable. Many times decisionmakers rely on models to guide their environmental management choices, especially when costly decisions are involved and the problem and solution involve complex relationships. This is exemplified by the decision of the Long Island Sound Hypoxia Management Conference (see Case Study for Long Island Sound). Generally, empirical and mathematical models are the most widely used models that statistically or mathematically relate nutrient loads or concentrations to important ecological response variables (e.g., dissolved oxygen deficiency, algal blooms and related decrease in water clarity, and loss of seagrasses). They both depend on the scientific robustness and accuracy of underlying conceptual models.

This chapter addresses both empirical and mathematical models. Considerably more space is devoted to mathematical models, because they are capable of addressing many more details of underlying processes when properly calibrated and validated. They also tend to be more useful forecasting (extrapolation) tools than simpler models, because they tend to include a greater representation of the physics, chemistry, and biology of the physical system being modeled (NRC 2000). A great danger in complex mathematical models is that error propagation is difficult to explicitly measure, and there is a tendency to use a more complex model than required, which drives costs up substantially and unnecessarily. Another consideration that is gaining acceptance is that mathematical models need to be appropriately scaled to spatial and temporal processes, or they may suffer problems similar to empirical models when one extrapolates the results of scaled experiments to full-sized natural systems. Also, empirical coefficients introduced into equations often hide the degree of uncertainty concerning the fundamental nature of the processes being represented.

Use of Empirical Models in Nutrient Criteria Development

Statistical models are empirical and are derived from observations. To be useful as predictive tools, relationships must have a basis in our understanding, typically represented by conceptual models. However, extrapolation from empirical data is known to be uncertain. Thus, these models are most reliable when used within the range of observations used to construct the model. When shown to meet program objectives and requirements, empirical models are a desirable place to begin model development and, if later determined to be required, they often provide insights into the structure needed for development of mathematical models. Empirical models typically are useful if only a subsystem of the larger ecosystem is of primary interest.

Frequently, the impression is given that the only credible water quality modeling approach is that of mathematical process-based dynamic computer modeling. This is not the case. For example, a Tampa Bay water quality modeling workshop in 1992 (Martin et al. 1996) produced the consensus recommendation that a multipronged (mechanistic and empirical) modeling approach be implemented to provide technical support for the water quality management process. The Tampa Bay National Estuary Program produced an empirical regression-based water quality model. The estimated N loads were related to observed chlorophyll concentrations using the regression model (Janicki and Wade 1996):

$$C_{t,s} = \alpha_{t,s} + \beta_s * L_{t,s}$$

where $C_{t,s}$ = average chlorophyll *a* concentration at month t and segment s,

$L_{t,s}$ = total N load at month t and segment s,

$\alpha_{t,s}$ and β_s are regression parameters.

A related model equated Secchi depth to average chlorophyll *a* concentrations (Greening et al. 1997). This analysis was followed by an empirical model that related N loadings to in-bay chlorophyll *a* concentrations.

There are many other examples of empirical models used to relate environmental forcing functions to ecological responses, especially nutrient load/concentration and response relationships. Much of the professional aquatic ecological literature reports on use of empirical models (e.g., Chapters 2 and 3). Empirical models have their limitations, but when judiciously applied, they offer a highly useful tool to water quality managers.

Use of Mathematical Models in Nutrient Criteria Development

Mathematical models can play an important role in assessing acceptable nutrient loads and concentrations in estuaries and near-coastal areas. For example, models are used to:

- Develop a relationship between external nutrient loads and resulting nutrient concentrations, which can then be used to define allowable loads
- Define the relationship between nutrient concentrations and other endpoints of concern, such as biomass or dissolved oxygen
- Provide an increased understanding of the factors affecting nutrient concentrations, such as the relative importance of point and nonpoint source loads
- Simulate relationships between light attenuation and expected depth of sea grass growth

The intent of this section is to describe the models available for assessing the relationship between nutrient loading and nutrient-related water quality criteria for estuaries and near-coastal waters. This chapter provides general guidance and some specific procedures for selecting and applying an appropriate model. It is divided into the following sections: (1) Model Identification and Selection, (2) Model Classification, (3) Use of Models for Nutrient Investigation, and (4) Management Applications.

Extensive EPA guidance (i.e., U.S. EPA 1985, 1990a-c; 1997; EPA document # 841-B-97-006) currently exists on these topics. This section serves primarily to condense the existing guidance with some modifications, to reflect changes in the science that have occurred subsequent to their publication. In addition, emphasis is placed on the simpler, more empirical techniques that are applied most easily. Readers are referred to the original guidance materials for more detailed discussions of the concepts described in this section.

9.2 MODEL IDENTIFICATION AND SELECTION

The first steps in the modeling process are model identification and selection. The goals are to identify the simplest model(s) that addresses all of the important phenomena affecting the water quality problems, and to select from those the most useful analytical formula or computer model. Selection of too simple a model can result in predictions of future water quality that are too uncertain to achieve the decisions or objectives of the study. On the other hand, selection of an overly complex model may also result in misdirected study resources, delays in the study, and increased cost. Predictive uncertainty may increase to unacceptable levels because of model parameters that cannot be adequately estimated with available data. Study costs will increase because of the additional data requirements and the expanded computer and staff time needed for model runs, analysis, and sensitivity studies.

Model Identification

Model identification entails four basic steps:

- Establish study objectives and constraints
- Determine water quality pollutant interactions
- Determine spatial extent and resolution
- Determine temporal extent and resolution

Each is discussed below.

Study Objectives and Constraints

The first step in identifying an appropriate model for a particular site is to clearly delineate the objectives of the modeling analysis. These objectives address questions such as:

- What are the nutrients of concern?
- What are the environmental endpoints of concern?
- What spatial and temporal scales are adequate for management concern?
- What management issues must the model address?
- What is the acceptable level of uncertainty in model predictions?

The nutrients of concern addressed in this document are nitrogen or phosphorus (depending on which is the limiting nutrient or will become limiting after controls are implemented). Environmental endpoints of concern are total nutrient concentration and other indicators of excessive nutrients such as chlorophyll/biomass and minimum dissolved oxygen. Local, State, and Federal regulations contribute to the definition of objectives by specifying time and space scales that the model must address: for example, the averaging period, or the season at which the criteria are applicable.

All expected uses of the model are to be stated clearly in advance. If the model will be used to predict future allowable nutrient loads, the specific conditions to be evaluated must be known. Then a final study objective is established that pertains to the required degree of reliability of model predictions, which may vary depending on whether the model application is designed for screening level estimation or for more detailed predictions.

The reliability objective is directly related to project constraints, as there is often a mismatch between desired model reliability and available resources. Resource constraints can cover four areas: data, time, level of effort, and expertise. Appropriate model selection must be balanced between competing demands. Management objectives typically favor a high degree of model reliability, but resource constraints generally prohibit the degree of reliability desired. Decisions often are required regarding whether to proceed with a higher-than-desired level of uncertainty, or to postpone modeling until additional resources can be obtained.

Water Quality/Pollutant Interactions

After the pollutants and water quality indicators are identified, the significant water quality processes must be determined. These processes directly or indirectly link the pollutants to be controlled with the primary water quality indicators. All other interacting water quality constituents thought to be significant should be included at this point. This consolidation can best be seen in a diagram or flow chart representing the mass transport and transformations of water quality constituents in a defined segment of water. Figure 9-1 illustrates variables and processes important to the eutrophication process. Not all of these need to be included in the actual model selected for use. Those excluded, however, should be considered externally and reflected in the coefficients.

At the end of this step all the available knowledge of a system should be assimilated in a way that permits major water quality processes and ecological relationships to be evaluated for inclusion in the numerical model description. This conceptual model is the starting point from which systematic reductions in complexity can be identified to provide an adequate representation of the system while meeting the objectives of the study.

The simplest level of model complexity considers only total nutrient concentrations and assumes that all of the processes shown in Figure 9-1 either have no effect on total nutrient concentrations (as is sometimes assumed for total nitrogen), or can be lumped into a single overall loss coefficient.

Models that simulate phytoplankton concentrations or dissolved oxygen typically include all of the processes shown in Figure 9-1, and sometimes many more, to describe such processes as sediment diagenesis and competition among multiple phytoplankton classes. Denitrification in the model is expressed in terms of the water column carbonaceous biochemical oxygen demand (CBOD).

Spatial Extent and Scale

Two spatial considerations must be addressed in the model identification process: spatial extent and scale. Spatial extent pertains to the specific boundaries of the area to be assessed. Spatial scale pertains to the number of dimensions to be considered and the degree of resolution to be provided in each dimension.

Several guidelines can help locate proper model boundaries. In general, the boundaries should be located beyond the influence of the discharge(s) being evaluated. Otherwise, proper specification of boundary concentrations for model projections is very difficult. Boundaries should be located where flow or stage and water quality are well monitored. Upstream boundaries should be located at a fall line, or at a gaging station in free-flowing, riverine reaches. Downstream boundaries are best located at the mouth of an estuary, or even nearby in the ocean. For large estuaries with relatively unaffected seaward reaches, the downstream boundary can be located within the estuary near a tidal gage and water quality monitoring station.

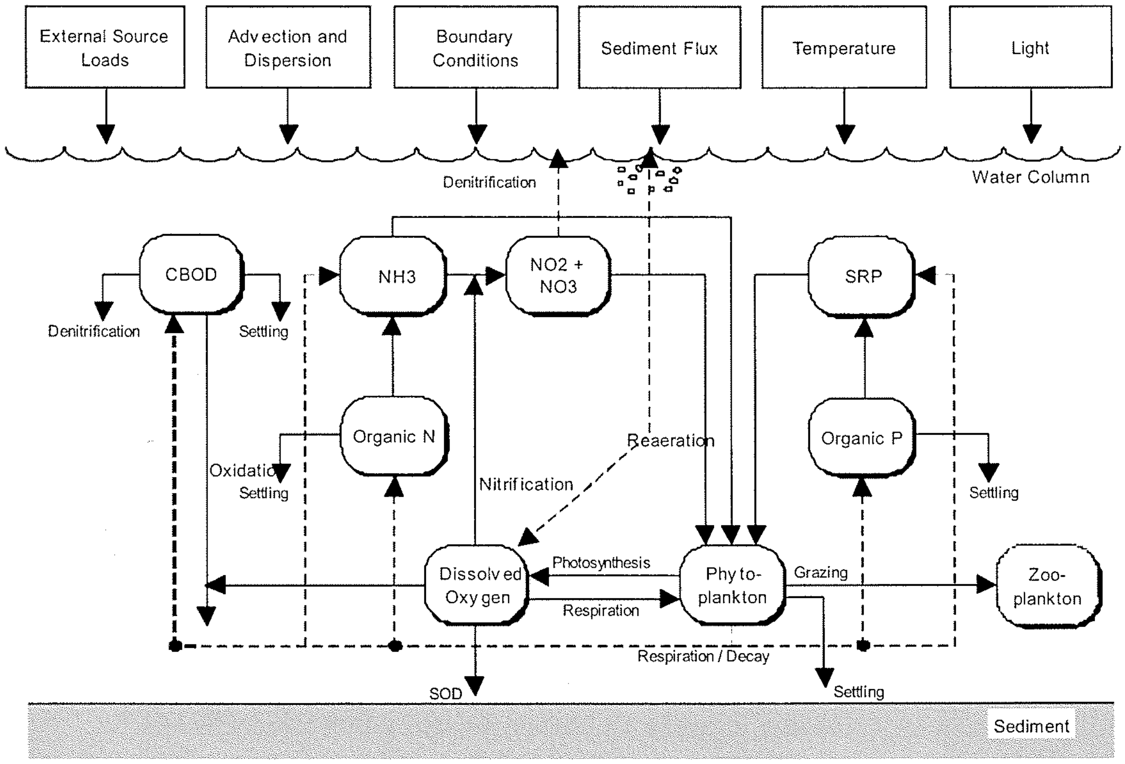

Figure 9-1. Eutrophication model framework : an example of hypoxia-based conceptual framework for water quality model. Source: Bierman et al. 1994.

Appropriate model spatial scale requires consideration of two factors: (1) the extent to which spatial gradients in water quality occur and (2) the extent to which these variations need to be considered from a management perspective. Real estuaries and near-shore waters all exhibit three-dimensional properties. There are gradients in hydrodynamic and water quality constituents over length, width, and depth. The effective dimensionality of an estuary includes only those gradients that affect the water quality analysis significantly.

One-dimensional models consider the change in pollutant concentration over a single dimension in space, typically oriented longitudinally down the length of an estuary. Two-dimensional models can consider concentration gradients in the lateral and longitudinal directions (termed x-y orientation), or concentration gradients that occur longitudinally and vertically (termed x-z orientation). Three-dimensional models describe changes in concentration that occur over all three spatial dimensions. These models provide the most detailed assessment of pollutant distribution with respect to a discharge; they also have the most extensive model input requirements and are the most difficult to apply.

Justifiable reductions in dimensionality result in savings in model development, simulation, and analysis costs. Usually the vertical and/or lateral dimension is neglected. Eliminating a dimension from the water quality analysis implies acceptable uniformity of water quality constituents in that spatial dimension. For example, use of one-dimensional models implies acceptably small deviations in concentration from the cross-sectional mean, both vertically and laterally. This judgment requires understanding both the transport behavior of estuaries and the specific objectives of the study.

Spatial variations are best determined by plotting observed water quality concentrations versus distance along the dimensions of concern. If such data are not available, other types of methods are available to estimate the importance of spatial variations. These are described in U.S. EPA (1990a) and discussed briefly here. The methods can be divided into three categories:

- Relatively simple desktop methods that compare the stratification potential caused by freshwater inputs to the mixing potential caused by tides and other currents
- Dye studies that observe the degree of mixing
- Geomorphological classification, which categorizes estuaries and the degree of mixing based on standard morphological categories (e.g., drowned river valleys)

Two situations exist where the observed spatial variations can be ignored. The first is when the primary location of water quality concern occurs in an area where these gradients are not important. A good example would be a nutrient modeling study to consider the impacts of a discharge on phytoplankton. If it takes 2 miles for a bankside discharge to undergo complete lateral mixing, but the location of maximum algal density is 5 miles downstream, lateral variability in water quality need not be described by the model. The second situation where a known gradient need not be modeled is where management objectives are not concerned with the gradient. Examples of this include water quality standards that are expressed on a spatially averaged basis.

The choice of spatial scale and layout of the model network requires considerable judgment. Knowledge of the regulatory problem must be combined with knowledge of the loading, transport, and transformation processes and an understanding of the model chosen to perform the simulations. Competing factors often must be balanced, such as precision and cost, or the better fit of one section of the network versus another.

Temporal Extent and Scale

The temporal resolution of water quality models falls into one of two broad categories, steady state or dynamic (i.e., time-variable). Steady-state models predict pollutant concentrations that are expected to result from a single set of loading and environmental conditions. Dynamic models predict changes in water quality over time in response to time-variable loads and environmental conditions.

Steady-state models are much easier to apply and require considerably fewer resources than dynamic models. This ease of application makes them the preferred modeling framework when loading to the system can be assumed to be constant and information on changes in concentration over time is not required. Potential uses of steady-state models include calculation of seasonal average total nutrient concentrations in response to seasonal average loads. Steady-state models also have been used to predict "critical condition" low-flow phytoplankton densities. Steady-state models are poorly suited for evaluating individual intermittent events (i.e., runoff) but can be used to evaluate the cumulative effect of multiple, intermittent events on a seasonal basis.

The timeframe to be represented for a particular steady-state simulation (e.g., monthly average, seasonal average) must be longer than the water residence time (flushing time) of the estuary. The water residence time is the time required to remove a parcel of water from an upstream location in an estuary. Factors that control flushing include tidal action, freshwater inflow, and wind stress. Typical flushing times range from days in small estuaries, or those dominated by tributary flow, to months in large estuaries during low tributary flow conditions. Several formulae have been used to estimate flushing times. The Fraction of Fresh Water Method, the Tidal Prism Method, and the Modified Tidal Prism Method are fully discussed in Mills et al. (1985) and briefly described in the following section.

Dynamic models should be used when information on changes in concentration over time is required. Dynamic models can be divided into two categories, quasi-dynamic and fully dynamic. Quasi-dynamic simulations predict variations on the order of days to months. The effects of tidal transport are time-averaged, and net or residual flows are used. Fully dynamic simulations predict hour-to-hour variations caused by tidal transport.

The duration of dynamic simulations can range from days to years, depending on the size and transport characteristics of the study area, the reaction kinetics and forcing functions of the water quality constituents, and the strategy for relating simulation results to the regulatory requirements. One basic guideline applies in all cases: the simulations should be long enough to eliminate the effect of initial conditions on important water quality constituents at critical locations. Flushing times provide the minimum duration for simulations of dissolved, nonreactive pollutants. The annual sunlight and temperature cycles almost always require that eutrophication simulations range from seasons to years.

Predicting the year-to-year eutrophication response of large estuaries is best accomplished by quasi-dynamic simulations. In general, if the regulatory need or kinetic response is on the order of hours, then fully dynamic simulations are required; if regulatory needs are long-term averages and the kinetic response is on the order of seasons to years, then quasi-dynamic or steady-state simulations are preferred.

Model Selection

The goal of model selection is to obtain a simulation model that effectively meets all study objectives. In the final analysis, how a model is used is more important to its success than exactly which model is used. Nevertheless, although selection of an appropriate model will not guarantee success, it will help. Selection of an inappropriate model will not guarantee failure, but will render a successful outcome more difficult.

Models may be classified in different and somewhat arbitrary ways. Some models may not quite fit in any category, or may fit well in several. In addition, models tend to evolve with use. The exact capabilities of the individual models described here may change. In particular, pollutant fate processes may be modified. Usually the computational framework and the basic transport scheme remain stable over time. For this reason, transport characteristics will provide the basis for the model classification scheme used here. Models selected for discussion here are general purpose, in the public domain, and available from or supported by public agencies.

9.3 MODEL CLASSIFICATION

Estuarine and near-coastal models consist of two components: hydrodynamics and water quality. Although the hydrodynamic component is independent of the water quality component, water quality depends on the transport processes controlled by hydrodynamics. As a result, estuarine models can be classified as Level I to Level IV, according to the temporal and spatial complexity of the hydrodynamic component of the model.

Level I includes desktop screening methodologies that calculate seasonal or annual mean total nutrient concentrations based on steady-state conditions and simplified flushing time estimates. Steady-state models use an unvarying flow condition that neglects the temporal variability of tidal heights and currents. These models are designed for relatively simple screening level analyses. They also can be used to highlight major water quality issues and important data gaps in the early model-identification stage of a more complex study.

Level II includes computerized steady-state or tidally averaged quasi-dynamic simulation models, which generally use a box or compartment-type network. Tidally averaged models simulate the net flow over a tidal cycle. These models cannot predict the variability and range of nutrient concentrations throughout each tidal cycle, but they are capable of simulating variations in tidally averaged concentrations over time. Level II models can predict slowly changing seasonal water quality with an effective time resolution of 2 weeks to 1 month.

Level III includes computerized one-dimensional (1-d) and quasi two-dimensional (2-d) dynamic simulation models. These real-time models simulate variations in tidal heights and velocities throughout each tidal cycle. One-dimensional models treat the estuary as well-mixed vertically and laterally. Quasi 2-d models employ a link-node approach that describes water quality in two dimensions (longitudinal and lateral) through a network of 1-d nodes and channels. Tidal movement is simulated with a separate hydrodynamic package in these models. The required data and modeling resources typically are unavailable to support models of Level III or above on a widespread basis.

Level IV consists of computerized 2-d and 3-d dynamic simulation models. Dispersive mixing and seaward boundary exchanges are treated more realistically than in the Level III 1-d models. These models are almost never used for routine nutrient assessment, because of excessive resource requirements.

Level I Models

Level I desktop methodologies may be employed using a hand-held calculator or computer spreadsheet and are based on steady-state conditions, first-order decay coefficients, simplified estimates of flushing time, and seasonal pollutant concentrations. The EPA screening methods provide a series of Level I analyses as described below.

EPA Screening Methods

WQAM is a set of steady-state desktop models that includes both one-dimensional and two-dimensional box model calculations (Mills et al. 1985). Specific techniques contained in WQAM are the Fraction of Freshwater Method, the Modified Tidal Prism Method, Advection-Dispersion Equations, and Pritchard's Two-Dimensional Box Model.

Fraction of Freshwater Method

The Fraction of Freshwater Method estimates pollutant concentrations in one-dimensional estuaries from information on freshwater and tidal flow by comparing salinity in the estuary with salinity in the local seawater. The fraction of freshwater at any location in the estuary is calculated by comparing the volume of freshwater at that location with the total volume of water:

$$fx = \frac{S_s - S_x}{S_s} \qquad (9\text{-}1)$$

where f_x = fraction of freshwater at location x, S_s = seawater salinity at the mouth of the estuary, and S_x = salinity at location x.

This ratio can be viewed as the degree of dilution of the freshwater inflow (as well as pollutants) by seawater. With this in mind, the total dilution of a pollutant input can be calculated by multiplying the seawater dilution by the freshwater dilution. This then provides a simple way to calculate concentrations of conservative pollutants. For any location x, at or downstream of the discharge, pollutant loads are diluted by tidal mixing and upstream flows. The amount of dilution can be calculated by:

$$C_x = f_x \frac{W}{Q} \qquad (9\text{-}2)$$

where C_x = constituent concentration at location x at or downstream of discharge, f_x = fraction of freshwater at location x, W = waste loading rate (mass/time), and Q = freshwater inflow (volume/time).

The right side of Equation 9-2 can be divided into two distinct terms. The term W/Q represents the classical equation for determining dilution in rivers caused by upstream flow. The second term, f_x, accounts for the further dilution of the river concentration by tidal influx of seawater.

Concentrations upstream of the discharge are estimated from the concentration at the point of mix and the relative salinity of the upstream location. The upstream concentrations are assumed to be diluted by freshwater to the same degree that salinity is diluted. The equation is:

$$C_x = f_d \frac{W}{Q} \frac{S_x}{S_d} \tag{9-3}$$

where f_d = fraction of freshwater at discharge location, S_x = salinity at upstream location x, and S_d = salinity at discharge location.

The fraction of freshwater at the discharge location, f_d, is determined by applying Equation 9-1 at the discharge location. Equation 9-3 can be modified to assess the impact of nutrients entering from the seaward boundary by replacing the leading f_dW/Q term with the boundary nutrient concentration.

Cumulative pollutant impacts from multiple sources are obtained through a two-step process. First, pollutant concentration caused by each source independent of all other discharges must be determined. This determination is accomplished by applying Equation 9-2 or 9-3, one discharge at a time, for any estuary location of interest. The second step is to determine the total concentration at that location. This determination is accomplished by adding all of the incremental concentrations caused by each discharge, as calculated in the first step. This process can be repeated for any location of interest.

The Fraction of Freshwater Method can be used to predict cumulative impacts in one-dimensional (i.e., narrow) systems with significant freshwater inflow. Upstream freshwater flow must be large with respect to total pollutant inflow for this method to be applicable. The method assumes conservative pollutant behavior. It is consequently best used to investigate total nitrogen concentrations, because overall loss rates of total nitrogen from the water column generally are small.

Modified Tidal Prism Method

The Modified Tidal Prism Method estimates dilution from the total amount of water entering an estuary. It is more powerful than the Fraction of Freshwater Method because it can consider not only tidal dilution but also nonconservative reaction losses. It is best applied to investigate total nutrient concentrations, but provides additional flexibility to describe pollutant losses that may occur through settling or denitrification.

The method divides an estuary into segments whose lengths and volumes are calculated using low-tide volumes and tidal inflow. The tidal prism (i.e., total volume of tidal inflow) is compared for each segment with the total segment volume to estimate flushing potential in that segment over a tidal cycle. The Modified Tidal Prism Method assumes complete mixing of the incoming tidal flow with the water resident in each segment.

The Modified Tidal Prism Method requires seven inputs:

- Freshwater inflow to the estuary
- Salinity of seawater at the downstream boundary
- Pollutant loading rate
- Salinity of each segment
- Low-tide volume for each segment
- Intertidal volume (tidal prism) for each segment
- First-order constituent loss rate for each segment

The first step of the method is to segment the estuary. This requires an initial time-consuming step of dividing the estuary into segments with lengths equal to the distance traveled by a particle over a tidal cycle. Cumulative subtidal and intertidal water volumes must be plotted for the estuary, and a graphical procedure is used to define model segmentation. Once the estuary has been segmented, a series of calculations can be performed to estimate constituent concentrations in each segment. Specific methods for dividing the estuary and performing the calculations are provided in Mills et al. (1985).

Advection-Dispersion Equations

Analytical equations have been developed to predict the concentration of nonconservative constituents in one-dimensional estuaries. These types of equations consider the processes of net seaward flows (advection) and tidally averaged mixing (dispersion), as well as simple decay. They can be used to predict total nutrient concentrations at various locations in an estuary in response to alternative nutrient loading rates. One-dimensional advection-dispersion equations can be expressed in several different forms (O'Connor 1965), with the most common form contained in the water quality assessment methodology. These equations require numerous simplifying assumptions, such as constant geometry and tidal mixing along the length of the estuary, but have proven to be a useful screening tool.

The advection-dispersion equations require five inputs: upstream freshwater flow rate (R), constituent loading rate (W), estuarine cross-sectional area (A), tidally averaged dispersion coefficient (E), and first-order decay rate coefficient (k). The first three inputs can be measured directly. The latter two inputs must be determined indirectly through the model calibration process described below. Two equations are provided, one which predicts concentrations at any distance (x) upstream of the discharge of concern and another for concentrations at any distance seaward of the discharge. Co is the concentration at the point of discharge. The equations are:

$$C = C_0 e^{j_2 x} \quad X > 0 \text{ (down estuary)} \qquad (9\text{-}4)$$

$$C = C_0 e^{j_1 x} \quad X < 0 \text{ (up estuary)}$$

where:

$$j_2 = \frac{R}{2AE}\left(1-\sqrt{1+\frac{4kEA^2}{R^2}}\right)$$

$$j_1 = \frac{R}{2AE}\left(1+\sqrt{1+\frac{4kEA^2}{R^2}}\right)$$

$$C_0 = \frac{W}{R}\frac{1}{\sqrt{1+(4kE/U^2)}}$$

These equations can be used to evaluate multiple loading sources by independently applying Equation 9-4 for each loading source and summing the predicted concentrations across the estuary.

Pritchard's Two-Dimensional Box Model
Vertically stratified estuaries add a significant degree of complexity to the modeling analysis. Pritchard (1969) developed a relatively simple approach, which can predict nutrient concentration distributions along the length of an estuary in both an upper and lower layer. This approach is based on numerous simplifying assumptions, including:

- Steady-state conditions
- Conservative pollutant behavior
- Uniform constituent concentration within each layer or each segment

The following information is required: (1) freshwater flow rate into the head of the estuary, (2) pollutant mass loading rates, and (3) longitudinal salinity profiles along the length of the estuary in the upper and lower layers. The method solves a series of linear equations describing the salinity balance around each segment to determine net flows and dispersion between each segment. Specific methods for performing the calculations are provided in Mills et al. (1985).

Results from Pritchard's model can be used to directly calculate conservative constituent concentrations throughout the estuary or to serve as the hydrodynamic input to one of the Level II models described below.

Level II Models

Level II models include computerized steady-state and tidally averaged simulation models that generally use a box or compartment-type network. Steady-state models are difficult to calibrate in situations where hydrodynamics and pollutant releases vary rapidly. Consequently, these models are less appropriate when waste load, river inflow, or tidal range vary appreciably with a period close to the flushing time of the waterbody. Level II models are the simplest models available that are capable of describing the relationship between nutrient loads and some of the endpoints of concern of the eutrophication process (i.e., chlorophyll *a*, minimum dissolved oxygen).

The Level II models by EPA are QUAL2E and the Water Quality Analysis Simulation Program (WASP5), with its associated eutrophication program EUTRO5.

QUAL2E

QUAL2E is a steady-state, one-dimensional model designed for simulating conventional pollutants in streams and well-mixed lakes (U.S. EPA 1995) and is not recommended for estuaries. Rather, QUAL TX, which allows tidal boundary conditions, may be more appropriate, but documentation on this model is very sparse.

WASP6.0

The Water Quality Analysis Simulation Program (WASP6.0) is a general, multidimensional model that utilizes compartment modeling techniques (Ambrose et al. 1993). The equations solved by WASP6.0 are based on the principle of conservation of mass. Operated in the quasi-dynamic mode, WASP6.0 requires the user to supply initial segment volumes, network flow fields, and inflow time functions. The user also must calibrate dispersion coefficients between compartments. WASP6.0 has the capability of simulating nutrient-related water quality issues at a wide range of complexity.

EUTRO5

EUTRO5 is the submodel in the WASP6.0 system that is designed to simulate conventional pollutants. EUTRO5 combines a kinetic structure adapted from the Potomac Eutrophication Model with the WASP transport structure. EUTRO5 predicts DO, carbonaceous BOD, phytoplankton carbon and chlorophyll *a*, ammonia, nitrate, organic nitrogen, organic phosphorus, and orthophosphate in the water column and, if specified, the underlying bed. In addition to segment volumes, flows, and dispersive exchanges, the user must supply deposition and resuspension velocities for organic solids, inorganic solids, and phytoplankton. Rate constants and half-saturation coefficients for the various biochemical transformation reactions must be specified by the user. Finally, the time- and/or space-variable environmental forcing functions, such as light intensity, light extinction, wind speed, cloud cover, temperature, and benthic fluxes, must be input.

Level III Models

Level III includes computerized 1-d and 2-d models that simulate variations in tidal height and velocity throughout each tidal cycle. Level III models enable characterization of phenomena varying rapidly within each tidal cycle, such as pollutant spills, stormwater runoff, and batch discharges. Level III models also are deemed appropriate for systems where the tidal boundary impact, as a function of the hydrodynamics and water quality, is important to the modeled system within a tidal period.

Tidally varying (intratidal) models have found most use in the analysis of short-term events, in which the model simulates a period of time anywhere from one tidal cycle to a month. Some seasonal simulations also have been conducted.

In using Level III models, one must decide whether a 1-d longitudinal system is sufficient, or whether a 2-d model is required to capture the longitudinal and lateral variations in the estuary. For estuaries whose channels are longer than their width and reasonably well mixed across their width, a 1-d model may be chosen. If large differences exist in water quality from one side of an estuary to the other, or if vertical stratification is important, then a 2-d model is appropriate.

All Level III models considered here can simulate nutrient-eutrophication interactions. These models also include settling rates and benthic flux rates for several different constituents, such as phosphorus, nitrogen, and sediment oxygen demand. The Level III model distributed by EPA is the WASP6.

Level IV Models

Level IV includes a variety of computerized 2-d and 3-d dynamic simulation models. Dispersive mixing and seaward boundary exchanges are treated more realistically than in the Level III 1-d models. Although not routinely used in nutrient analyses, they are now finding use by experts in special studies. Level IV models are required when variations in concentrations in all three dimensions are of concern. The time-variable nature of a Level IV model ensures the need for a time-variable watershed model in order to provide for the nonpoint source inputs. Fully 3-d models that can predict longitudinal, lateral, and vertical transport are the most complex and expensive to set up and run.

At present, no Level IV model is supported by EPA. Three current Level IV models, CE-QUAL-W2, Integrated Compartment Model (ICM), and EFDC, are described below.

CE-QUAL-W2

CE-QUAL-W2 is a dynamic 2-d (x-z) model developed for stratified waterbodies (Environmental and Hydraulics Laboratories 1986). This is a U.S. Army Corps of Engineers modification of the Laterally Averaged Reservoir Model (Edinger and Buchak 1983; Buchak and Edinger 1984a,b). CE-QUAL-W2 consists of directly coupled hydrodynamic and water quality transport models. Hydrodynamic computations are influenced by variable water density caused by temperature, salinity, and dissolved and suspended solids. Developed for reservoirs and narrow, stratified estuaries, CE-QUAL-W2 can handle a branched and/or looped system with flow and/or head boundary conditions. With two dimensions depicted, point and nonpoint loadings can be distributed spatially.

CE-QUAL-W2 simulates as many as 20 other quality variables. Primary physical processes included are surface heat transfer, shortwave and longwave radiation and penetration, convective mixing, wind- and flow-induced mixing, entrainment of ambient water by pumped-storage inflows, inflow density current placement, selective withdrawal, and density stratification as influenced by temperature and dissolved and suspended solids. Major chemical and biological processes in CE-QUAL-W2 include the effects on DO of atmospheric exchange, photosynthesis, respiration, organic matter decomposition, nitrification, and chemical oxidation of reduced substances; uptake, excretion, and regeneration of phosphorus and nitrogen and nitrification-denitrification under aerobic and anaerobic conditions; carbon cycling and alkalinity-pH-CO_2 interactions; trophic relationships for total phytoplankton; accumulation and decomposition of detritus and organic sediment; and coliform bacteria mortality.

CH3D-ICM

CH3D is a 3-d, finite-difference hydrodynamic model, developed by the U.S. Army Corps of Engineers Waterways Experiment Station (WES) in Vicksburg, MS. Results from CH3D have been linked to the ICM to model water quality in the Chesapeake Bay. The ICM was developed as the integrated-compartment eutrophication model component of the Chesapeake Bay model package. The model contains detailed eutrophication kinetics, modeling the carbon, nitrogen, phosphorus, silica, and dissolved oxygen cycles.

CH3D-ICM is a linkage of CH3D, a hydrodynamic model, and ICM, a water quality model. CH3D is a hydrodynamic model developed for the Chesapeake Bay Program (Johnson et al. 1991). The model can be used to predict system response to water levels, flow velocities, salinities, temperatures, and the three-dimensional velocity field. CH3D makes hydrodynamic computations on a curvilinear or boundary-fitted platform grid. Deep navigation channels and irregular shorelines can be modeled because of the boundary-fitted coordinates feature. Vertical turbulence is predicted by the model and is crucial to a successful simulation of stratification, destratification, and anoxia. A second-order model based on the assumption of local equilibrium of turbulence is employed.

ICM is a finite-difference water quality model that may be applied to most waterbodies in one, two, or three dimensions (Cerco and Cole 1995). The model predicts time-varying concentrations of water quality constituents and includes advective and dispersive transport. The model also considers sediment diagenesis benthic exchange. ICM incorporates detailed algorithms for water quality kinetics. Interactions among state variables are described in 80 partial-differential equations that employ more than 140 parameters. An improved finite-difference method is used to solve the mass conservation equation for each cell in the computational grid and for each state variable.

EFDC

EFDC is a linked three-dimensional, finite-difference hydrodynamic and water quality model developed at the Virginia Institute of Marine Sciences (Hamrick 1996). EFDC contains extensive water quality capabilities, including a eutrophication framework based on the ICM model. EFDC is a general-purpose hydrodynamic and transport model that simulates tidal, density, and wind-driven flow; salinity; temperature; and sediment transport. Two built-in, full-coupled water quality/eutrophication submodels are included in the code.

EFDC solves the vertically hydrostatic, free-surface, variable-density, turbulent-averaged equations of motion and transport; transport equations for turbulence intensity and length scale, salinity, and temperature in a stretched, vertical coordinate system; and horizontal coordinate systems that may be Cartesian or curvilinear-orthogonal. Equations describing the transport of suspended sediment, toxic contaminants, and water quality state variables also are solved.

The model uses a finite-difference scheme with three time levels and an internal-external mode splitting procedure to achieve separation of the internal shear, or baroclinic, mode from the external free-surface gravity wave, or barotropic, mode. An implicit external-mode solution is used with simultaneous computation of a two-dimensional surface elevation field by a multicolor successive overrelaxation procedure. The external solution is completed by calculation of the depth-integrated barotropic velocities using the new surface elevation field. Various options can be used for advective transport, including the "centered in time and space" scheme and the "forward in time and upwind in space" scheme.

Summary of Model Capabilities

The important features of the models selected for discussion in this manual are summarized in Tables 9-1 and 9-2. The information provided in these tables is primarily qualitative and sufficient to determine whether a model may be suitable for a particular application. For complete information, consult the appropriate user's manuals, the supporting agency, and other experienced users.

9.4 USE OF MODELS FOR NUTRIENT INVESTIGATION

This section describes procedures for using models to perform nutrient assessment in estuaries and near-coastal waters. It describes the model calibration and validation process, where model parameters that best describe the waterbody of interest are selected. In addition, guidance is provided on using models for nutrient management and assessment.

The first subsection describes a general procedure for calibrating nutrient models, and briefly describes the validation procedure used to estimate the uncertainty of such models. The subsection also describes some statistical methods for testing the calibrated models. These methods are useful to aid in the various calibration phases and also in the validation phase to measure how well model predictions and measurements of water quality agree.

The second subsection provides guidance on the management application of a calibrated model. Methods to project effects of changes in waste loads and to determine causes of existing conditions are discussed. Finally, a case study application is provided.

Model Calibration and Validation

Model calibration is the process of determining model parameters most appropriate for a given site-specific application. Calibration of a model involves a comparison of the measured and simulated receiving water quality conditions. The nature of the model calibration process depends upon the complexity of the model selected. Simpler models contain relatively few parameters that need to be calibrated, whereas more complex models contain many.

Calibration alone is not adequate to determine the predictive capability of a model for a particular estuary. To map out the range of conditions over which the model can be used, one or more additional independent sets of data are required to determine whether the model is predictively valid. This model validation exercise defines the limits of usefulness of the calibrated model. Without validation testing, the model merely describes the conditions defined by the calibration data set. The degree of uncertainty of any projection or extrapolation of the model remains unknown.

Table 9-1. Basic model features

Methods/Model	Time Scales	Spatial Dimensions	Hydro-dynamics	Data Expertise Requirements	Distributing Agency	Scale of Effort
Fraction of Freshwater	SS	1D	0	Minimal	EPA	Days
Modified Tidal Prism	SS	1D	0	Minimal	EPA	Days
Advection-Dispersion Equations	SS	1D	0	Minimal	EPA	Days
Pritchard's 2-D Box Model	SS	2D (xz)	0	Minimal	EPA	Days
QUAL2E	SS	1D	I	Moderate	EPA	Few months
WASP5	Q/D	1D, 2D (xy), or 3D	I, S	Moderate to substantial	EPA	Few months
CE-QUAL-W2	D	2D (xz)	S	Substantial	Army Corps	Several months
CH3D-ICM	D	3D	S	Extreme	EPA	Months to years
EFDC	D	3D	S	Extreme	EPA	Months to years

D - dynamic; Q - quasi-dynamic (tidal-averaged); SS - steady state; x - 1-dimensional, xy - 2-dimensional, longitudinal-lateral; xz - 2-dimensional, longitudinal-vertical; xyz - 3-dimensional; B - compartment or box 3d; xx - link node branching 2d; 0 - No hydraulics specified, inferred from salinity data; I - hydrodynamics input; S - hydrodynamics simulated.

In general, models are calibrated in phases, beginning with the selection of the model parameters and coefficients that are independent of parameters to be calibrated later. For purposes of this discussion, the process is divided into the categories of hydrodynamic calibration and water quality calibration. The discussion covers the parameters that need to be calibrated for each level of model as well as the specific model outputs to be used for the calibration comparison. Calibration of the more complex models requires detailed guidance; the reader is referred to other documents (e.g., U.S. EPA 1990b; Thomann and Mueller 1987) for a discussion that is more comprehensive than is feasible here.

Hydrodynamic Calibration

The first phase of calibration concentrates on the hydrodynamic and mass transport models. Two Level I models, the Fraction of Freshwater Method and the Tidal Prism Method, have no hydrodynamic parameters that require calibration. In these simplest cases, all hydrodynamic and mass transport processes are implicitly considered via specification of observed salinity values. Although there are no parameters to calibrate for these models, there is merit in testing the model's predictive validity by comparing predicted concentrations with field observations of a conservative (i.e., nondecaying) substance, if such data are available.

For the remaining Level I and Level II models, only one hydrodynamic parameter requires calibration: the tidal dispersion coefficient. It is possible to calibrate the hydrodynamic and mass transport portions of these models by determining values for this coefficient that best describe observed salinity or conservative tracer measurements.

Table 9-2. Key features of selected models

Model	Key Features	Advantages	Disadvantages/ Limitations
WQAM	Simplified equations to simulate dilution, advection, dispersion, first-order decay, empirical relationships between nutrient loading, and total nutrient concentration	Few data requirements; can be employed easily with a hand calculator or computer spreadsheet	Limited to screening and midlevel applications
QUAL2E	Steady-state model provides adequate simulation of water quality processes, including DO-BOD and algal growth cycles	User-friendly Windows interface; widely used and accepted; able to simulate all of the conventional pollutants of concern	Limited to simulation of time periods during which stream flow and input loads are essentially constant
WASP5	Based on flexible compartment modeling approach; can be applied in 1, 2, or 3 dimensions	Has been widely applied to estuarine situations; considers comprehensive DO and algal processes; can be used in 3-d simulations by linking with hydrodynamic models	Coupling with multi-dimensional hydrodynamic models requires extensive site-specific linkage efforts
CE-QUAL-W2	Uses an implicit approach to solve equations of continuity and momentum; simulates variations in water quality in the longitudinal and lateral directions	Simulates the onset and breakdown of vertical stratification; most appropriate where vertical variations are an important water quality consideration	Application requires extensive modeling experience
CH3D-ICM	Finite-difference model can be applied to most water bodies in 1 to 3 dimensions; predicts time-varying concentrations of constituents; includes advective and dispersive transport	State-of-the-science eutrophication kinetics	Computationally intensive; requires extensive data for calibration and verification; requires a high level of technical expertise to apply effectively
EFDC	Linked 3-d, finite-difference hydrodynamic and water quality model contains extensive water quality capabilities; water quality concentrations can be predicted in a variety of formats suitable for analysis and plotting	3-d description of water quality parameters of concern; entire range of hydrodynamic, sediment, eutrophication, and toxic chemical constituents can be considered	Computationally intensive; requires extensive data for calibration and verification; requires a high level of technical expertise to apply effectively

Level III models typically contain two calibration parameters, the channel roughness coefficient and the dispersion coefficient. Occasionally these models are calibrated with current velocity and water surface elevation data, but more often are indirectly calibrated from salinity or conservative tracer measurements that also must be used to calibrate the mass transport model. Indirect calibration can result in an imprecise description of both the circulation and mass transport algorithms, but this is not a severe drawback unless the critical water quality components of the waste load allocation model are sensitive to small changes in circulation and mass transport.

Level IV hydrodynamic models contain several calibration parameters, including bottom and surface friction coefficients; vertical, lateral, and horizontal eddy viscosity coefficients; and wind speed coefficients. Calibration efforts for these types of models are beyond the scope of this document.

Kinetic Process Calibration

The second phase of calibration involves selection of the set of kinetic coefficients describing nutrient cycles and other aspects of the eutrophication process. Again, the effort required is directly related to the complexity of the model selected.

Two Level I models—the Fraction of Freshwater Method and Pritchard's model—have no kinetic parameters that require calibration. The models assume that constituent concentrations undergo no kinetic processes that affect their concentration, and typically are appropriate only for estimating total nitrogen concentrations. The remaining Level I models can describe nonconservative constituents, and lump all kinetic processes into a single overall decay coefficient. Model calibration in these cases consists of a comparison of predicted versus observed total nutrient concentrations.

The calibration of higher level nutrient and phytoplankton models requires significant expertise because of the complexity of the interactions between a number of the components of the cycles involved.

Coefficients that require calibration in these models pertain to: transformation rates among various forms of a given nutrient; maximum phytoplankton growth rates; phytoplankton respiration rates; phytoplankton growth sensitivity to light and nutrients; and phytoplankton and detrital settling velocities.

Model Validation

Validation testing is designed to confirm that the calibrated model is useful at least over the limited range of conditions defined by the calibration and validation data sets. The procedure is not designed to validate a model as generally being useful in every estuary, or even as useful over an extensive range of conditions found in a single estuary. Validation, as employed here, is limited strictly to indicating that the calibrated model is capable of producing valid results over a limited range of conditions. Those conditions are defined by the sets of data used to calibrate and validate the model. As a result, it is important that the calibration and validation data cover the range of conditions over which predictions are desired.

Validation testing is performed with an independent data set collected during a second field study. The field study may occur before or after the collection of calibration data. For the best results, however, the validation data should be collected after the model has been calibrated. This schedule of calibration and validation ensures that the calibration parameters are fully independent of the validation data. Often it is difficult to assemble the necessary resources to conduct the desired number of surveys. Therefore, it is important that surveys be scheduled in an innovative manner and the choice of calibration and validation data sets remain flexible to make the test of the calibrated model as severe as possible.

Too often, limited studies attempt calibration but not validation. This approach, in effect, limits the study to describing the conditions during the calibration data collection period and increases the uncertainty associated with the waste load allocation. In fact, model prediction uncertainty cannot be reliably assessed in these cases.

Model Testing

During and after the calibration and validation of a model, at least two types of testing are important. First, throughout the calibration procedure, a sensitivity test helps determine which parameters and coefficients are the most important. Second, a number of statistical tests help define the extent of agreement between model simulations and measured conditions.

The sensitivity analysis is simply an investigation of how much influence changes in model coefficients have on simulated results. Typically, important coefficients, parameters, boundary conditions, and initial conditions are varied by a positive or negative constant percentage to see what effect the change has on critical predictions. The coefficients and parameters are changed one at a time and the effects typically are ranked to show which parameters have the most influence and which have the least.

The second type of testing involves assessment of the "goodness of fit" for model simulations, compared with measurement of important water quality parameters. In addition to making a visual assessment, a number of statistical tests have proven useful. These include root mean square error, relative error, and regression analysis. Other more detailed statistical analyses are described in U.S. EPA (1990b).
The root mean square (rms) error is a criterion that is widely used to evaluate the agreement between model predictions. The rms error can be defined as:

$$rms = \left[\Sigma \left(C_m - C_s \right)^2 N \right]^{0.5} \qquad (9\text{-}5)$$

where C_m = measured concentration, C_s = simulated concentration, and N = number of measurements.

The rms error can be used to compute simultaneous discrepancies at a number of points, or it can be used to compute discrepancies between measurements and predictions at a single point over time. Global rms errors can be computed for a series of measurements at multiple points over time.

When discrepancies between model simulations and measurements are not uniform over parts of the estuary or over time, the relative error may be a more appropriate statistic for testing calibration or validation. The relative error is defined as:

$$e = \left|\overline{C}_m - \overline{C}_s\right| \Big/ \overline{C}_m \qquad (9\text{-}6)$$

where the overbars denote the average measured or simulated value. Averages can be performed over multiple sites or over time. The relative error behaves poorly for small values of measurements if discrepancies are not proportional to the magnitude of the measurement (i.e., small values of C_m magnify discrepancies) and if $C_m > C_s$ (as the maximum relative error is usually taken to be 100%). Therefore, the relative error is best for computing composite statistics when discrepancies are not constant, as may occur when calibration over an extensive range is attempted.

Regression analysis is very useful in identifying various types of bias in predictions of dynamic-state variables. The regression equation is written as:

$$C_m = a + bC_s + \varepsilon \qquad (9\text{-}7)$$

where a = intercept value, b = slope of the regression line, and ϵ = the error in measurement mean, C_m. The standard linear regression statistics computed from the above equation provide insight into the goodness of fit for a calibration. The square of the correlation coefficient, r^2, measures the percent of the variance accounted for between measured and predicted values. The slope estimate, b, and intercept, a, can indicate any consistent biases in the model calibration. A model calibration that perfectly described all available data would have a correlation coefficient of 1.0, a slope of 1:1, and a zero intercept.

9.5 MANAGEMENT APPLICATIONS

Once the model is calibrated and validated, it can be used to simulate future conditions to determine effects of changes in waste loads or to investigate causes of existing problems. This section describes three types of management application: (1) load-response analysis, (2) determination of acceptable nutrient loads, and (3) investigation of causes of nutrient problems.

Load-Response Analysis

A load-response analysis consists of performing multiple model simulations using different loading rates and examining the water quality predicted for each simulation. The most common use of a model to investigate nutrients in estuaries is to determine the water quality throughout an estuary in response to changes in nutrient loads. Models are designed to predict water quality based on loadings and environmental conditions (Figure 9-2).

This type of analysis also requires specification of the environmental conditions (e.g., freshwater inflows, tidal conditions) to be considered. The results of the load-response analysis are directly related to the environmental conditions specified for the model simulation. For example, use of summer-average environmental conditions in the model will show the response in summer-average water quality to changes in loads. For the simplest Level I models, environmental conditions are specified implicitly through the use of salinity observations. Predictions from these models will correspond to the environmental conditions that were in effect when the salinity was measured. The more complex models require explicit definition of environmental condition and can be used to provide predictions for a wide range of environmental conditions.

Acceptable Nutrient Loads

The most common use for water quality models is to define allowable loads necessary to achieve water quality objectives. As seen in Figure 9-2, models predict water quality for a specified set of loads and environmental conditions. Determination of acceptable loads typically requires an iterative procedure, as shown in Figure 9-3. The first iteration consists of performing a model simulation using existing loads and comparing predicted water quality with objectives. Assuming that the existing loads result in unacceptable water quality, additional model simulations are performed using incremental reductions in nutrient loads until water quality objectives are achieved.

The approach shown in Figure 9-3 can be used to define necessary reductions in total loads as well as reductions in individual contributors to the total load.

The results of the above approach are highly dependent on the environmental conditions selected, as allowable loading rates can vary substantially across different environmental conditions. Two approaches are available for selecting critical conditions for use in defining allowable loads. These approaches are termed the critical conditions approach and the continuous simulation approach. In the critical conditions approach, a single set of environmental conditions is selected for analysis. These conditions typically represent critical or worst-case conditions, that is, those environmental conditions that will result in the poorest water quality for a given set of loads. The rationale for the critical conditions approach assumes that if loads are defined to meet water quality objectives during "critical" conditions, the same loads will result in attaining water quality objectives during most other conditions as well.

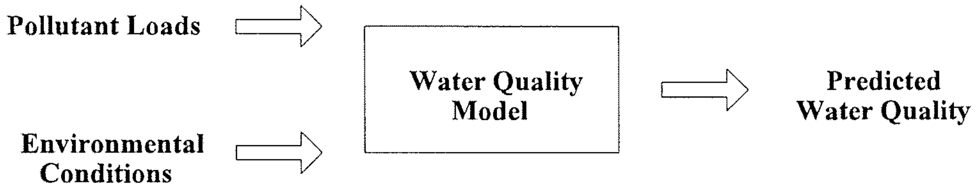

Figure 9-2. Use of models in load-response analysis.

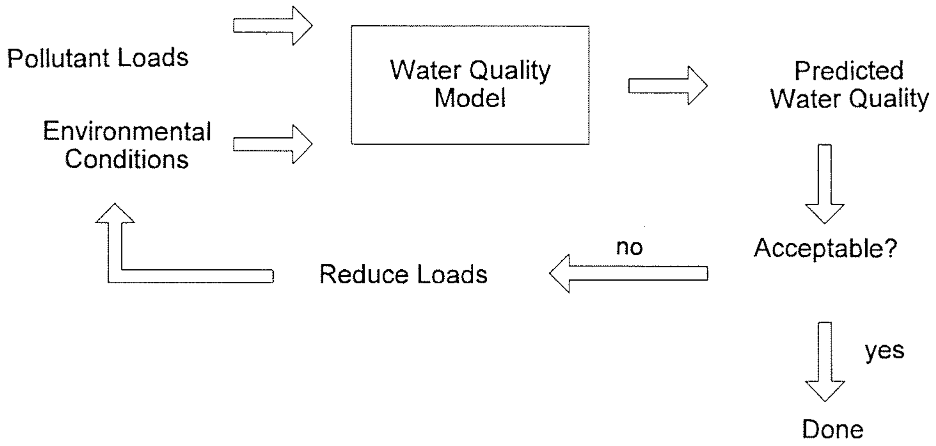

Figure 9-3. Use of models in determining allowable loads.

The continuous simulation approach performs simulations for as long a duration as is feasible, using historically observed variations in environmental conditions. The predicted water quality resulting from the continuous simulation is analyzed to determine the frequency with which water quality problems are observed to occur.

The overall intent of the modeling analysis is to define loads that will restrict the occurrence of water quality problems to an acceptable frequency. Each of the above two methods has particular strengths and weaknesses for performing this task. The continuous simulation approach provides a direct means to consider frequency of occurrence (i.e., number of years per problem) but has extreme resource requirements. The ability to perform continuous simulation of sufficient duration typically is constrained by the availability of data describing historical environmental conditions, or by computational requirements for the higher level models. The critical conditions approach has much more manageable resource requirements; however, there are no clear methods to establish appropriate critical conditions. In estuaries, freshwater, tides, wind, and other factors all can affect water quality. Selection of appropriate values for each environmental parameter requires considerable judgment. Furthermore, the specific level of protection associated with any single set of environmental conditions cannot be evaluated without performing a continuous simulation.

Case Study Example

Water quality models also can be used to gain an increased understanding of the relative importance of various loading sources to an estuary or near-coastal water. It is possible to investigate the contribution of individual loading sources to the water quality problem by performing a series of simulations examining each loading source separately. Because most water quality models assume a linear relationship between pollutant load and resulting water quality impact, it is possible to determine overall impacts to the estuary by summing the impacts from each source.

Investigation of Causes of Nutrient Problems

Shipps Creek (Figure 9-4) is a long, narrow, tidal tributary receiving nutrient inputs from upstream runoff and a single wastewater treatment plant (WWTP). This case study example demonstrates the use of models to perform three tasks:

- Estimate the contribution of various loading sources to the overall summer-average total nitrogen concentration
- Estimate the effect of a 50% reduction in loads from the WWTP on total nitrogen concentrations throughout the estuary
- Estimate the reduction in loading necessary to achieve an average total nitrogen concentration of 0.100 mg/L in the lower half of the estuary

Short-term answers were required, and screening-level accuracy was judged acceptable because of the short timeframe and limited data available.

The Fraction of Freshwater Method was selected because the estuary was considered one-dimensional, long-term average results were acceptable, and the water quality target was specified in terms of total nutrient levels.

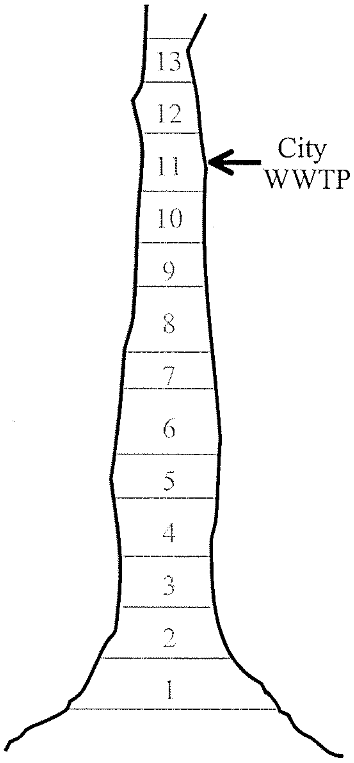

Figure 9-4. Shipps Creek site map and salinity monitoring location.

Information available to support the study included summer-average salinity measurements at 13 locations along the length of the estuary, summer-average freshwater inflows and total nitrogen loads to the estuary, nitrogen loads from the WWTP, and nitrogen and salinity concentrations outside of the estuary. This information was compiled as shown in Table 9-3 to allow implementation of the Fraction of Freshwater Method. The top two rows of Table 9-3 show the measured loading rates and seaward boundary conditions. The two leftmost columns define segments centered around each of the salinity measurements. The third column applies Equation 9-1 to calculate the fraction of freshwater in each segment.

The fourth through sixth columns in Table 9-3 apply Equations 9-2 or 9-3 as appropriate to determine the incremental contribution to the total nitrogen (TN) concentrations from each of three possible contributing sources: upstream (TN_{UP}), wastewater treatment plant (TN_{WWTP}), and the downstream seaward boundary (TN_{SEA}). Equation 9-2 is applied only to those segments downstream of the loading source, whereas Equation 9-3 is applied to those segments upstream of the loading source. Equation 9-2 is applied to all segments for examining impacts from upstream sources, whereas Equation 9-3 is applied to all segments for examining impacts from the seaward boundary. For determining WWTP impacts, Equation 9-2 is applied to segments 1-11 and Equation 9-2 is applied to segments 12-13. The final column in Table 9-3 sums the incremental contributions from each of the sources to provide a prediction of overall TN concentrations throughout the estuary.

Table 9-3. Calculation spreadsheet for Shipps Creek estuary

Freshwater Inflow		**Seawater Salinity**	**Upstream Load**	**WWTP Load**	**Seawater TN**	
Q = 100,000 cmd		**Ss = 30 ppt**	**W = 5,000 g/day**	**W = 500,000 g/day**	**0.005 ppm**	
Segment #	Salinity, S_i (ppt)	Fraction of Freshwater, f_i	TN_{UP} (mg/L)	TN_{WWTP} (mg/L)	TN_{SEA} (mg/L)	Overall TN (mg/L)
1	29	0.03	0.002	0.017	0.005	0.023
2	27	0.10	0.005	0.050	0.005	0.060
3	25	0.17	0.008	0.083	0.004	0.096
4	23	0.23	0.012	0.117	0.004	0.132
5	21	0.30	0.015	0.150	0.004	0.169
6	19	0.37	0.018	0.183	0.003	0.205
7	18	0.40	0.020	0.200	0.003	0.223
8	16	0.47	0.023	0.233	0.003	0.259
9	14	0.53	0.027	0.267	0.002	0.296
10	12	0.60	0.030	0.300	0.002	0.332
11	10	0.67	0.033	0.333	0.002	0.368
12	5	0.83	0.042	0.110	0.001	0.152
13	1	0.97	0.048	0.025	0.000	0.074

The results of this modeling analysis are shown graphically in Figure 9-5, showing the overall TN distribution as well as its component. Although the Fraction of Freshwater Method does not require calibration, it would be worthwhile at this point to confirm that the model predictions of TN throughout the estuary were consistent with observed data collected over the same time period. Figure 9-5 shows that the WWTP is the dominant source of nitrogen throughout most of the estuary. Upstream sources are the dominant component only at the extreme head of the estuary. Nitrogen contributions from the seaward boundary are small throughout the system. The results in Table 9-2 and Figure 9-4 satisfy the first objective of this study, which was to determine the contribution of various loading sources to the overall summer-average total nitrogen concentration. The second objective of the study was to determine the water quality resulting from a 50% reduction in WWTP TN loads. This was accomplished by reapplying Equations 9-2 and 9-3 using one-half of the original WWTP loads. Results of this analysis are shown in Figure 9-6, indicating a decrease in peak TN concentrations from 0.368 to 0.202 mg/L and a decrease in lower estuary (defined as segments 1-6) average concentrations from 0.111 to 0.064 mg/L. This nearly 50% reduction in concentrations was expected, because the original analysis had demonstrated that the WWTP was the dominant loading source to the estuary.

The final objective of the study was to determine the loading reductions necessary to achieve a lower estuary average concentration of 0.08 mg/L. No single answer exists to this question, because three separate sources of nitrogen to the estuary contribute to the total concentration. Analysis of the data in Table 9-3 shows that the incremental contribution of the upstream, WWTP, and seaward sources to lower estuary average concentrations were 0.010, 0.100, and 0.004 mg/L, respectively. Because the seaward

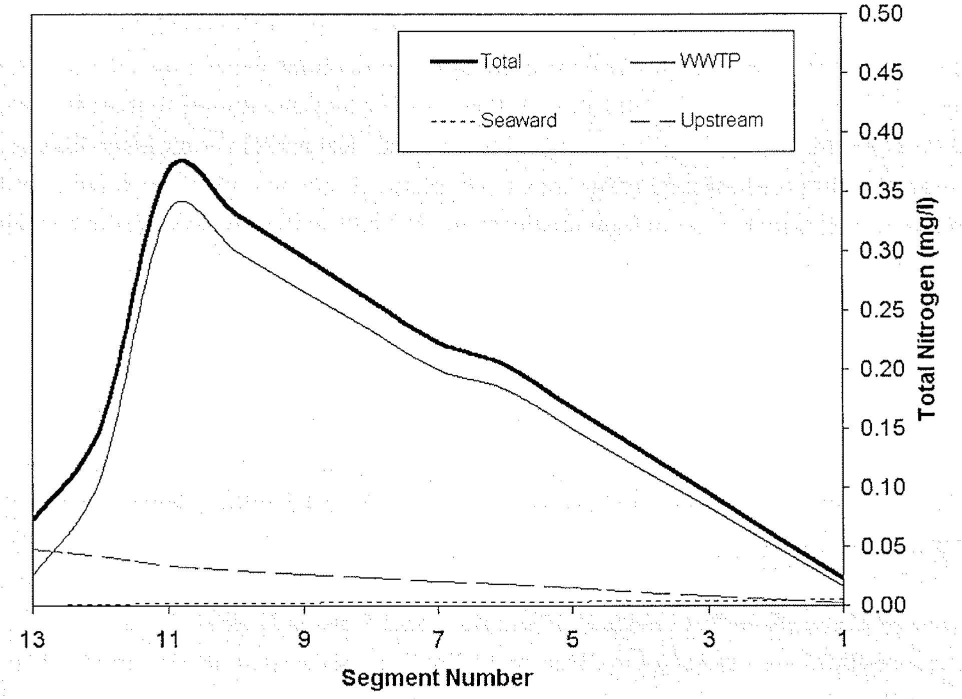

Figure 9-5. Model results for existing conditions.

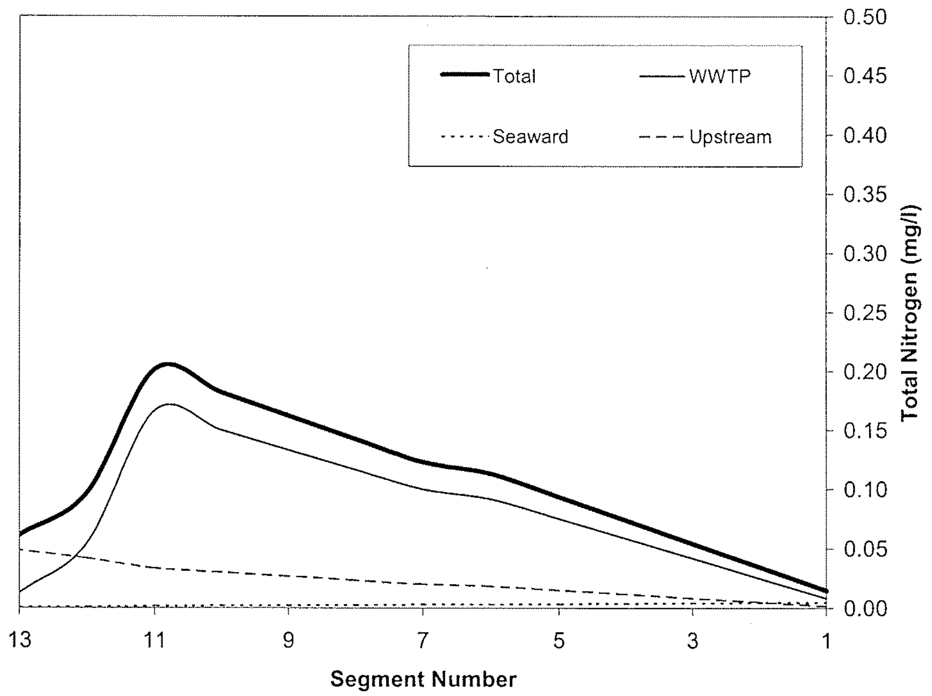

Figure 9-6. Model results for 50% reduction in WWTP load.

boundary nitrogen concentration cannot be controlled, management reductions must be restricted to either the upstream sources or the WWTP. The WWTP load must be reduced by at least 20% to meet the target TN concentration of 0.080 mg/L; otherwise, its contribution alone will exceed the target. Beyond the initial 20% reduction in the WWTP source, further reductions must come either from the WWTP or upstream sources. The specific allocation of these load reductions among sources is an economic and social decision that the model is not designed to address. The model is expressly designed, however, to test alternative proposals of load reductions to determine if they will meet the water quality objective. For example, a 25% reduction in both upstream and WWTP sources resulted in an average concentration of 0.087 mg/L (i.e., above the target), but a 30% reduction in WWTP loads coupled with a 40% reduction in upstream loads was shown to just meet the target.

All model simulations presented here should be viewed with extreme caution, because they are based on an uncalibrated, screening-level model. The level of uncertainty for these predictions cannot be quantified and is expected to be quite large. The model results do, however, provide the best possible estimate describing the relationship between nutrient loads and resulting concentrations, given the available resources.

Overview of Chesapeake Bay Airshed, Watershed, and Estuary Models

The cross-media models used in the Chesapeake Bay analysis consist of three models: an airshed model, a watershed model, and a model of the Chesapeake estuary. These models are linked so that the output of one simulation provides input data for another. The simulation period is the 10-year period of January

1, 1985, to December 31, 1994. Versions of these models have been used by the Chesapeake Bay Program for more than a decade and have been refined and upgraded several times.

Airshed Model

The Chesapeake Bay Program airshed model provides estimates of atmospheric deposition loads of nitrogen. A product of the EPA National Exposure Research Laboratory in Research Triangle Park, North Carolina, RADM (pronounced "radum") is an acronym for Regional Acid Deposition Model. RADM is a three-dimensional model that tracks nutrient emissions across the eastern United States. Two RADM grids meet various resolution needs. A large grid scale covers the entire RADM domain and contains 20,000 square cells of 6,400 square kilometers each. A fine grid scale covers the region of the Chesapeake Bay watershed and has 60,000 cells, each covering 400 square kilometers. The model domain in the vertical is 15 cells deep, reaching from ground level to the top of the free troposphere. The depth of the cells increases with altitude. One of the findings of the RADM model is that the Chesapeake Bay airshed, defined as the area accounting for 75% of the deposition in the watershed, is approximately 5.5 times the size of the watershed.

RADM is used to drive scenarios associated with reductions in atmospheric deposition of nitrogen. A base condition deposition represents an estimate of the current condition of atmospheric deposition in the watershed and is developed from a regression of National Atmospheric Deposition Program (NADP) data. RADM scenarios of atmospheric deposition reductions are incorporated into Watershed Model scenarios by adjusting the base NADP condition on a segment-by-segment basis with a percent change prescribed by RADM scenario results. Results from RADM specify loads of wet and dry deposition to the Chesapeake watershed for the State Implementation Program (SIP) and Limit of Technology scenarios. Deposition loads are input directly to the land surfaces of the watershed model or to the tidal water surface of the Chesapeake Bay estuary model package as daily loads of wet deposition (from rain washout of atmospheric nitrate and ammonia) and 12-year average loads of dry deposition.

Three atmospheric deposition loads were used for the Chesapeake analysis: (1) the base condition of atmospheric deposition, (2) the estimated atmospheric deposition of nitrogen equivalent to the 1998 SIP controls of atmospheric deposition, and (3) the estimated atmospheric deposition under full limit of technology control (see Table 9-4).

Table 9-4. Chesapeake watershed nitrogen deposition under varying management schemes for emissions of nitrogen atmospheric deposition precursors

Scenario	TN Deposition (millions of kg/year)
Base Condition	204
State Implementation Plan (SIP)	178
Limit of Technology	128

Sources: Chesapeake Bay Program Phase IV Watershed Model and RADM.

Watershed Model

The watershed model simulates nutrient and sediment loads delivered to the Chesapeake Bay from all areas of the watershed. Land uses of cropland, pasture, urban areas, and forests are simulated on an hourly time-step, tracing the fate and transport of input nutrient loads from atmospheric deposition, fertilizers, animal manures, and point sources. The simulation is an overall mass balance of nitrogen and phosphorus nutrients in the basin, so that the ultimate fate of input nutrients is simulated, either as incorporation into crop or forest plant material, incorporation into soil, or river runoff. Nitrogen fates included volatilization into the atmosphere and denitrification. Transport in rivers is simulated to the tidal waters of the Chesapeake Bay. Sediment is simulated as eroded material washed off land surfaces and transported to the tidal bay. Scenarios are run for 10 years on a 1-hour time-step, and results are aggregated into 10-year average loads for comparison among scenarios.

To simulate the delivery of nutrients and sediment to the bay, the watershed was divided into 86 major model segments, each with an average area of 194,000 hectares. Segmentation, based on three tiers of criteria, partitioned the watershed into regions of similar characteristics. The first criterion was segmentation of similar geographic and topographic areas, which were further delineated in terms of soil type, soil moisture holding capacity, infiltration rates, and uniformity of slope. The second criterion involved finer segmentation based on spatial patterns of rainfall. Each segment had a bank-full travel time of about 24–72 hours. The third criterion used to further delineate segments was based on features of the river reach. River reaches containing a reservoir were separated into a reservoir simulation and a river simulation of the free-flowing river. For example, the James basin had 11 model segments, 2 represented reservoirs on the James and Appomattox, and the segmentation generally became finer with closer proximity to tidal waters.

Model segments were located to take advantage of observed data locations, so that a model segment outlet was located close to monitoring stations. Water quality and discharge data were collected from Federal and State agencies, universities, and other organizations. More than 150 subsegments were used at the interface between the watershed and estuary models to accurately deliver flow, nutrient, and sediment loads to appropriate areas of the estuary. Increased simulation accuracy motivated the division of basins into multiple segments and into simulation time-steps of an hour, but all scenario results were reported at the level of the basin and for 10-year average loads.

The watershed model has been in continuous operation at the Chesapeake Bay Program since 1982 and has had many upgrades and refinements since that time. The watershed model used for this application was Phase 4.1 based on the HSPF Version 11 code (Hydrologic Simulation Program - Fortan - HSPF). Version 11 is a widely used public domain model supported by EPA, USGS, and the U.S. Army Corps of Engineers.

Estuary Model

The Chesapeake Bay Estuary Model Package (CBEMP) is actually several models simulating different aspects of water quality in the bay and tributaries. A water quality model simulates 22 parameters, or state variables, as listed in Table 9-5.

Table 9-5. Water quality state variables used in CBEMP

Temperature	Dissolved organic nitrogen
Salinity	Labile particulate organic nitrogen
Inorganic suspended sediments	Refractory particulate organic nitrogen
Diatoms	Total phosphorus
Cyanobacteria (blue-green algae)	Dissolved organic phosphorus
Other phytoplankton	Labile particulate organic phosphorus
Dissolved organic carbon	Refractory particulate organic phosphorus
Labile particulate organic carbon	Dissolved oxygen
Refractory particulate organic carbon	Chemical oxygen demand
Ammonium	Dissolved silica
Nitrate + nitrite	Particulate biogenic silica

Zooplankton were separated into two size classes: microzooplankton (>44 microns) and mesozooplankton (>202 microns).

Linked to the water quality model is a hydrodynamic model, simulating the hydrodynamics, or water movement, throughout the tidal estuary. The hydrodynamic model produced three-dimensional predictions of velocity, diffusion, surface elevation, salinity, and temperature on an intratidal time scale. The model grid of the hydrodynamic and water quality models consists of more than 10,000 cells.

The modeling process involves simulation of living resource parameters, such as dissolved oxygen, chlorophyll concentrations, and submerged aquatic vegetation (SAV). Computed parameters are compared with living resource standards, and an estimation is made of the degree to which computed conditions benefit the resources of interest (e.g., fish, oysters). In addition, the CBEMP includes the direct interactive simulation of SAV and water quality. Three phytoplankton groups were simulated.

Over seasonal time scales, the bay sediments are a significant source of dissolved nutrients to the overlying water column. The role of sediments in the systemwide nutrient budget is especially important in summer when seasonal low flows diminish riverine nutrient input. In addition, water temperatures enhance biological processes in the sediments, creating greater sediment oxygen demand. Bay sediments retain a long-term nutrient load "memory" of several years; that is, sediment nutrient fluxes to the water column are determined by organic nutrient inputs from several previous years. Therefore, the water quality model was coupled directly to a predictive benthic-sediment model. These two models interact at each time-step, with the water quality model delivering settled organic material to the sediment bed, and the benthic-sediment model calculating the flux of oxygen and nutrients to the water column.

Linked to the CBEMP are the watershed and airshed models, which provide daily input data. Generally, 10-year scenarios are run on 15-minute time-steps with output generated each 10 days. The estuary model has been in operation since 1987, with two major model refinements released since the initial 1987 steady-state model.

Further information on the entire suite of Chesapeake Bay Program models, their documentation, and application can be found at: http://www.chesapeakebay.net/model.htm.

CASE STUDY
NP BUDGET FOR NARRAGANSETT BAY

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808-956-8693
http://data.ecology.su.se/MNODE/North%20America/NRB.HTM

Narragansett Bay, Rhode Island (41° 35' N, 71° 20'W), is a relatively well mixed, near-oceanic salinity estuary on the northeast (Atlantic) coast of the U. S. It occupies an area of 264 km^2 (Table 1) and has a mean depth of 9.7 m. Note that both the area and volume differ from the comments in Nixon et al. (1995), but seem consistent with Kremer and Nixons (1978) explicit tabulation. Freshwater flow into the system averages about 8.2 x 10^6 m^3/d, from a watershed of 3500 km^2. Primary production in the system is dominated by phytoplankton (29 mol C m^{-2} yr^{-1}) with a C:N:P ratio of about 112:13:1. The budget described below is based on data collected primarily in the late 1970's and through much of the 1980's. Details of this kind of analysis can be found at the LOICZ - Biogeochemical Modelling web site at: http://data.ecology.su.se/MNODE/index.htm.

Sector area and volume data are from Kremer and Nixon (1978). Sector nutrient concentrations are annual averages (based on surface and deep water data) also from Kremer and Nixon. Sector nutrient masses are calculated as volume x concentration. The sectors at the bay mouth (#5, 8) are used for "oceanic values."

Nutrient exchange fluxes (Table 2) are calculated using an average 26-day exchange time, as calculated by Pilson (1985) with a water and salt budget (analogous to procedure in Gordon et al., 1996). The bay

Table 1. Sector areas, volumes, and nutrient concentrations. Data are used to calculate volume-averaged concentrations for the outer portion of the bay ("ocean") and the bay proper

SECT. #	VOL.10^6 m^3	AREA 10^6 m^2	DIP µM	NH4 µM	NO3 µM	Sum DIN µM	DIP 10^6 mol	NH$_4$ 10^6 mol	NO$_3$ 10^6 mol	S DIN 10^6 mol
1	130	20.1	1.8	12	11	23	0.23	1.56	1.43	2.99
2	300	44.6	1.5	7	6	13	0.45	2.10	1.80	3.90
3	115	28.5	1.6	3	6	9	0.18	0.35	0.70	1.05
4	463	61.9	1.4	4	4	8	0.65	1.85	1.85	3.70
5	204	20.0	1.0	1	3	4	0.20	0.27	0.60	0.87
6	222	26.0	1.2	2	5	7	0.27	0.44	1.11	1.55
7	573	38.5	1.0	2	4	6	0.57	1.15	2.29	3.44
8	554	24.2	0.7	1	2	3	0.39	0.39	1.11	1.50
SUM	2561	264								
		bay	1.3	4	5	9				
		ocean (secs. # 5,8)	0.8	1	2	3				

Table 2. Hydrographic exchange fluxes of nutrients

SOURCE OF FLUX	DIP 10^6mol/yr	NH_4 10^6mol/yr	NO_3 10^6mol/yr	DIN 10^6mol/yr
residual flow	-3	-7	-11	-18
net exchange flow	-18	-108	-108	-216
total hydrography	-21	-115	-119	-234

volume divided by the residence time gives a mixing exchange volume of 98.5 x 10^6 m^3/d, while the residual outflow equals the freshwater inflow (i.e., 8.2 x 10^6 m^3/d). It would, in principle, be possible to time-step through the data (at monthly increments, for example). However, to do that would require having the flow data to go with the nutrient data. Further, inspection of the graph by Nixon et al. (1995) of flow data and comparison of Pilson's (1985) flow—residence time regression equation suggests that the residence time over this range of flow is well approximated by a constant value for the exchange time. Various authors describe the bay as well mixed, and this is supported by the water composition data in Kremer and Nixon (1978). We therefore use a 1-box model to perform these calculations, rather than a vertically stratified model to describe hydrographic fluxes.

In Table 3, all boundary fluxes except hydrography were taken directly from by Nixon et al. (1985). Hydrographic flux was calculated as above. Δ Y's (the nonconservative fluxes) are calculated by difference (as described in Gordon et al., 1996). No data are available for DOP, DON, or for either inorganic or organic C, so the budget is based on inorganic N and P only. As discussed by Gordon et al. and consistent with comments in Nixon et al., it seems safe to assume that DOP and DON nonconservative fluxes do not contribute strongly to the overall nonconservative fluxes in this system.

Rates for the D Y's per unit area are calculated using the bay area of 264 km^2 (Table 4). Note that this area estimate is about 25% lower than the value used by Kremer and Nixon (1978). We have used the smaller area and volume on the basis that these are the data used to calculate the volume-averaged concentrations. Net (nfix-denit) is calculated on the assumption that the N:P ratio of D DIP is 13:1, then D DIN is balanced. Net (p-r) is calculated from the DIP flux, using a C:P ratio of 112:1.

Table 3. Total boundary fluxes of nutrients and inferred internal reactions—the system budget

Process	DIP 10^6mol/yr	NH_4 10^6mol/yr	NO_3 10^6mol/yr	DIN 10^6mol/yr
atmosphere	0	6	19	25
rivers	13	113	177	290
urban runoff	2	13	4	17
sewage	9	136	6	142
hydrography	-21	-115	-119	-234
D Y	-3	-153	-87	-240
(nfix-denit)				-201

Table 4. Nonconservative fluxes of materials and stoichiometrically inferred biogeochemical pathways

	DIP **mmol m^{-2} yr^{-1}**	**NH_4** **mmol m^{-2} yr^{-1}**	**NO_3** **mmol m^{-2} yr^{-1}**	**DIN** **mmol m^{-2} yr^{-1}**	**C** **mol m^{-2} yr^{-1}**
D Y	-11	-580	-329	-909	
D DIN_{exp}				-143	
(nfix-denit)				-766	
(p-r)					1.2

Nixon et al. (1995) have data with which the present budgetary estimates may be compared: They estimate DIP and DIN fluxes from the ocean to the bay by a hydrographic budget analogous to values used here for both influx and efflux, but they do not use this same hydrography to estimate nutrient fluxes to the ocean. Their inward DIP and DIN fluxes, obtained by time-stepping through the oceanic nutrient concentration data (bottom water only), are 27 and 115 x 10^6 mol/yr. The calculations here (using annual average data) are 29 and 108 x 10^6 mol/yr. The agreement is within 10%. It should be close, because both Nixon et al. and the calculations here are performing essentially the same calculation. Three points for minor disagreement would be that the values here just used a constant exchange rate (instead of time-varying); values used here were picked data off a graph; and surface and bottom values were averaged (on the graph, these are effectively identical in the outermost bay sectors).

Instead of using hydrography to estimate outward DIP and DIN flux, those authors estimate DIP and DIN fluxes from the bay to ocean by difference with other terms in their budget, to close the budget. They get 41-51 x 10^6 and 240-470 x 10^6 mol/yr. Again pulling the hydrographic terms apart, the calculations here yield 50 x 10^6 and 342 x 10^6 mol/yr (in both cases, within their range). It is worth noting that if the water exchange volume is incorrect, it would affect both influx and efflux of nutrients, hence have a relatively small effect on the difference between influx and efflux. The point here, of course, is that the difference between influx and efflux is probably more reliable than either of the individual fluxes.
Nixon et al. use a variety of considerations for two different sets of incubation data to assign baywide denitrification a range of 85-170 x 10^6 mol/yr (compared to 201 x 10^6 from the hydrographic budget; using their high values, agreement is within 20%).

Those authors estimate respiration to consume 8100 to 9200 x 10^6 mol/yr of organic C. Using their estimate for primary production (p) of 29 mol C m^{-2} yr^{-1} and the DIP-derived estimate for production - respiration (*p-r*) of 1.2, *r* is estimated to be 27.8 mol C m^{-2} yr^{-1}. Scaling by the bay area, this gives respiration to be 7340 x 10^6 mol/yr (within 20% of their lower estimate). If we were to use the are value given in Nixon et al. (328 km^2, instead of the value of 264 km^2 from Kremer and Nixon (1978), the respiration would be 9118 x 10^6 mol/yr (within their range).

Efforts to control the release of nutrients into Narragansett Bay have recently addressed nitrogen contributions from Publically Owned Treatment Works (POTWs) throughout the watershed. One nutrient reduction option currently being pursued is to maximize nitrogen removal from the final effluent by modifying operating conditions with existing equipment at the facility. Retrofitting existing facilities will also be considered where appropriate. A second venue involves drafting water quality based permit limits over the next few years to limit nitrogen in the final effluent of POTWs. Finally, a total maximum daily load (TMDL) for nitrogen is currently under development for the Providence River upstream of Narragansett Bay through the NPDES permitting process. A model is being developed that once calibrated, will set nitrogen load limits for POTWs that discharge to the river.

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