

A NUTRIENT-PHYTOPLANKTON-ZOOPLANKTON MODEL FOR CLASSIFYING
ESTUARIES BASED ON SUSCEPTIBILITY TO NITROGEN LOADS

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Abstract

Estuarine responses to nutrient loads can be remarkably different. Many driving variables including light, water residence time, physical stratification, and temperature are responsible for the diversity of the response. To classify estuaries based on their susceptibility to nutrient loads, a nutrient- phytoplankton- zooplankton (NPZ) model was developed and applied to river-dominated, well-mixed estuaries. Estuaries are classified as having low, medium, high and hyper eutrophic conditions by the model.

The result of the model suggests that water residence time is an important controlling variable in the process of achieving a steady-state response to nutrient loads. Although phytoplankton responses to residence time vary under different loads, they have the same positive trend. Phytoplankton responses are almost linear with water residence time initially, then decrease, and eventually plateau.

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Part1. Introduction

Eutrophication is defined as “an increase in the rate of supply of organic matter to an ecosystem” by Nixon (1995), which is also considered as a response of system productivity to nutrient enrichment (Carpenter et al. 1998). Economic development, population growth, and related human activities, such as various agricultural practices, wastewater treatment plants, urban runoff, and the burning of fossil fuels, have remarkably increased nutrient inputs by many times natural levels. These increases in nutrients often result in increased organic matter production and thus increased eutrophication. Increased nutrient inputs to coastal waters have led to substantial changes in coastal ecosystems in the United States and around the world, with an estimated degradation of two thirds of all U.S. coastal systems (Bricker et al.1999, NRC 2000).

In recent years, eutrophication has become a national, even global, concern. Many symptoms are present during eutrophication, for example, high chlorophyll *a* concentration, epiphyte abundance, loss of submerged aquatic vegetation, toxic algal blooms, and low dissolved oxygen. Many of these symptoms have been found from the Baltic, Adriatic, and Black Seas, to the estuaries and coastal waters of India, Japan, China, and Australia, and also in the United States, including the Chesapeake Bay, Long Island Sound, and the northern Gulf of Mexico (Bricker et al.1999). In recent years, almost all US estuaries have exhibited some level of eutrophic symptoms, although the scale, intensity and impacts vary widely, as do the levels of nutrient inputs that produce these symptoms (Bricker et al.1999).

Excess nutrients, the principal cause of eutrophication, can cause accelerated algal production. Nutrient inputs may also affect relative algae dominance as some species are favored at different nutrient concentration and ratios. Algal respiration and

algal debris decomposition can also deplete oxygen concentrations. When oxygen levels are significantly reduced, hypoxia can lead to significant reductions in the production of zooplankton and other aquatic animals. Increasing algal blooms can also block sunlight to submerged aquatic vegetation, which in turn inhibits their growth. Some toxic algal blooms may also increase because of the increasing nutrient inputs and changing nutrient ratios, and these toxins can affect the whole estuarine system. Tourism, boat manufacture, fisheries and other commercial activities that depend on the wealth of natural resources supplied by estuaries will also be affected.

To protect, restore, and manage coastal ecosystems, it is important to be able to predict their sensitivity to nutrient loads. While increased nutrient (nitrogen, phosphorus and silica) loads stimulate production of organic matter, principally in the form of phytoplankton and macroalgae, the scale and intensity of these eutrophication impacts vary widely among estuaries, even among those with the same nutrient load (NSTC, 2003). Because it is impractical to examine each estuary individually, it is important to develop an estuarine classification scheme based on estuarine susceptibility that can allow us to understand, predict, and manage eutrophication. In the following sections, key factors affecting the susceptibility to eutrophication are discussed.

Light availability

Light plays a critical role in controlling primary production and the susceptibility of estuaries to different nutrient loadings. Photosynthesis is a light-driven process that supports the transformation of nutrient elements and carbon dioxide into algal biomass, and is controlled by solar radiation. The amount of light available for photosynthesis limits the capacity of phytoplankton to assimilate and transform dissolved nutrients into new algal biomass. Therefore, when light availability is low,

phytoplankton growth can become limited by light rather than by nutrients (Nedwell et al. 2002).

A decrease in light intensity with increasing water depth is predominately due to the absorption of light by suspended particulate matter in an estuary. As concentrations of suspended particles increase, the aphotic depth increases at the expense of the photic depth. Therefore, as phytoplankton communities absorb light and grow, they can limit their own development through self-shading (Peterson and Festa, 1984).

Water residence time

The water residence time, an important physical control on ecological processes in an estuary, is defined as the mean time a parcel of water remains in the estuary.

Phytoplankton blooms can occur only when the phytoplankton turnover time, which is defined as the ratio of the standing stock to the integral production (Peterson and Festa, 1984), is shorter than the water residence time (NRC, 2000). If the water residence time is less than or equal to the phytoplankton turnover time, the algae are flushed from the system before they bloom. Since algal production cannot increase in this environment, eutrophication is prevented. In contrast, if the residence time is longer than the algae turnover time, there is sufficient time to assimilate nutrients, and for phytoplankton to accumulate. Algal sedimentation plays an important role in the relationship between water residence time and turnover time, because, even though water residence time is shorter than turnover time, algal biomass can still increase if it settles below the mixing layer before being flushing out. (Hopkinson, 1995)

Physical Stratification

Vertical stratification is controlled by the combination of waters with different

origins and densities. Coastal stratification is created by the presence of salinity gradients which are produced by the layering of denser, saltier shelf water below fresher surface water from rivers. However, wind and tidal stresses can upset the stabilizing effects and can be an important mechanism for the mixing of the upper and lower waters in estuaries. Coastal ecosystems also have a tidal current, which is one of the largest sources of energy mixing in coastal waters.

Vertical stratification can retain and increase phytoplankton blooms in the upper zone where light and nutrients are more favorable and thus encourage higher production as well as larger algal blooms. In addition, a vertically stratified system will also isolate deeper waters below the pycnocline from reaeration (NRC, 2000) and the diffusion of oxygen from the surface to the bottom. In a well-mixed system, however, oxygen and phytoplankton could mix to the lower layer, reducing the estuary's susceptibility to hypoxia.

Temperature

The rates of many reactions including photosynthesis and respiration change with temperature primarily because enzyme activity varies greatly with temperature. Most phytoplankton species have an optimal temperature range in which they can grow. For example, Bintz et al. (2003) showed that phytoplankton blooms are completely absent from cool unenriched mesocosms, and that warmer temperatures alone appeared to be capable of simulating phytoplankton blooms in warm unenriched systems. In addition, temperature is a major factor, along with salinity, affecting the depth of the mixing layer.

Part 2. Modeling Approaches

This section reviews examples of some estuarine models. Part 3 summarizes data sources and analysis of data characteristics. Part 4 describes the model used in this analysis. Model results and comparison with data are presented in Part 5. Conclusion and discussion are in Part 6.

Recognizing the factors affecting estuarine susceptibility to eutrophication is a prerequisite to developing a classification system for estuaries (NRC 2000). Modeling is a useful method for simulating the eutrophication process and evaluating the relative importance of various controlling factors. In addition, models, if well tested, can allow for prediction.

The purpose of this work was to develop a parsimonious model, capable of screening estuaries according to their susceptibility to nitrogen load variation, and to test this model against an expanded National Oceanic & Atmospheric Administration (NOAA) data set and observations from a wide range of estuaries.

Human activities can greatly alter the global cycling of nutrients, especially the movement of nutrients to estuaries and other coastal waters (NRC, 2000). Although a variety of changes may increase the productivity of freshwater and coastal marine ecosystems, it is clear that the most common single factor causing eutrophication in these environments is an increase in the amount of nitrogen and phosphorus they receive (Nixon, 1995). Despite the awareness of large-scale, long-term changes in river-estuarine watersheds, the consequences for the estuarine ecosystem of these activities are not fully understood (Charles et al. 1995). Improved models of these processes and their interactions can improve prioritizing systems for protection and remediation.

Scientific investigation of human disturbance of estuarine ecosystems has been

undertaken for only a few decades (Nixon, 1995), and the conceptual model of the problem is evolving rapidly. Based on various nutrient dynamic models, Cloern (2001) suggested three developmental phases of the conceptual models of the coastal eutrophication problem:

Phase I conceptual models were strongly influenced by the classical limnology approach, which was intensely studied in the 1960s. These models emphasized changing nutrient input as a signal, and responses to that signal as increased phytoplankton biomass and primary production, decomposition of phytoplankton-derived organic matter, and enhanced depletion of oxygen from bottom waters. However, estuarine ecosystems differ from lake ecosystems in terms of responses to nutrient input because of salinity, tidal fluxes and organisms. Although limnological models work for some estuaries, some important estuarine processes are missing because of the oversimplification. However, it is a good start for estuarine simulation of nutrient dynamics.

Phase II conceptual models reflect the differences between estuarine ecosystems and lake ecosystems and include explicit recognition of system-specific attributes to modulate the responses to enrichment. A complex suite of direct and indirect factors influence system responses, including linked changes in water transparency, the distribution of vascular plants and the biomass of macroalgae, sediment biogeochemistry and nutrient cycling, nutrient ratios and their regulation of phytoplankton community composition, the frequency of toxic or harmful algal blooms, habitat quality for metazoans, the reproduction and survival of pelagic and benthic invertebrates, and subtle changes such as shifts in the seasonality of ecosystem functions.

Phase III conceptual models are proposed by Cloern (2001) as guidance for

future work, organized around five questions that will shape coastal science in the early twenty-first century: “(1) How do system-specific attributes constrain or amplify the responses of coastal ecosystems to nutrient enrichment? (2) How does nutrient enrichment interact with other stressors (toxic contaminants, fishing harvest, aquaculture, nonindigenous species, habitat loss, climate change, hydrologic manipulations) to change coastal ecosystems? (3) How are responses to multiple stressors linked? (4) How does human-induced change in the coastal zone impact the Earth system as habitat for humanity and other species? (5) How can a deeper scientific understanding of the coastal eutrophication problem be applied to develop tools for building strategies at ecosystem restoration or rehabilitation?”

Below are outlined example of Phase I and Phase II models that have been developed in the last the decades.

A simple plankton model (Steele and Henderson, 1981)

This simple model was developed to provide insight into possible factors affecting plankton ecosystems. A qualitative understanding of nutrients (N), phytoplankton (P), and herbivores (H) are examined using the following three equations.

$$\frac{dN}{dt} = -\frac{N}{0.03 + N} * \frac{P}{1 + 2P} - 0.15P + \frac{160P^2}{1 + 800P^2} * H + 0.5H^2 + 0.03$$

$$\frac{dP}{dt} = (a - P)P - \frac{P^2}{1 + bP^2} H$$

$$\frac{dH}{dt} = \frac{cP^2}{1 + bP^2} H - dH^2$$

where a is the growth rate of phytoplankton, including effects of varying incident light and nutrient concentration; d is a variable coefficient, representing changes in predator population; c is the growth rate of herbivores; and b is the half maximum grazing coefficient.

Time lags were introduced into the predation term to simulate the consequences of the observed delay in the peak of predation rate compared with the herbivore peak. Despite its simplicity, the model explained the observations from the experiment. Ignoring the internal structure of each trophic level, it shows how changes in nutrient delivery can result in the alternations in growth rate.

Coastal ecosystem sensitivity to light and nutrient enrichment (Cloern 1999)

Developing general tools to estimate the susceptibility of coastal ecosystems to eutrophication, it is necessary to consider the physical processes that constrain the phytoplankton response to nutrient enrichment. For example, since the transformation of nutrients into algal biomass requires solar radiation as the energy source to drive photosynthesis, the expression of eutrophication can be constrained by the set of physical processes that govern the availability of sunlight energy to the phytoplankton. Therefore, besides nutrient limitation, light energy is another important factor controlling algae growth.

Cloern (1999) developed a growth-rate model to assess the relative importance of light energy in limiting algae growth. The model is designed to compare the response of growth rate to the change in nutrient load with the response of growth rate to the change in light availability. Growth ratio is defined as $R = (\partial\mu / \partial I') / (\partial\mu / \partial N')$, where μ is a certain growth rate, and I' and N' are light energy and nutrient concentration respectively. If R is greater than 1, phytoplankton growth rate is more sensitive to changes in light. If R is smaller than 1, it is more sensitive to changes in nutrient. This model was applied to North San Francisco Bay, South San Francisco Bay, Tomales Bay, and two Dutch estuaries: the Westerschelde Estuary and the eastern Oosterschelde Estuary. Strong light limitation was shown in the North San Francisco Bay and the Westerschelde Estuary, which corresponded to the high concentration of

nitrogen and phosphorous in the water. The South San Francisco Bay was a typical estuary where phytoplankton were limited by light availability from summer to winter but by nutrient availability in spring. The Tomales Bay and the Easeter Oosterschelde Estuary both indicated light limitation in winter but strong nutrient limitation from spring to autumn. This suggested that when algae started to bloom during spring and summer, nutrient supply was insufficient to sustain growth. However, given its emphasis on only light and nutrients, this model gives no information about estuarine susceptibility to other factors such as flushing time and mixing.

A model for partially mixed estuary (Peterson and Festa, 1984)

Peterson and Festa (1984) developed a two-dimensional steady-state model for light-driven phytoplankton productivity and biomass in partially mixed estuaries to examine effects of estuarine circulation and other environmental factors on phytoplankton development and distribution.

This model is set in x and z of Cartesian coordinate systems, where x represents the direction toward the river and z represents vertical position. The equation used to model phytoplankton is:

$$(bC)_t + (UC)_x + (WC)_z + (\omega bC)_z = (K_h bC_x)_x + (K_v bC_z)_z + b\{f_1[I, C, C^*] - f_2[C]\}$$

where $U=ub$, $W=wb$, u and w are the horizontal and vertical components of

velocity, respectively, b is the channel width, C is the concentration of particulate organic carbon, C^* is the concentration of suspended sediment, K_h and K_v are the horizontal and vertical exchange coefficients of salt. ω is the sinking velocity of the phytoplankton, f_1 and f_2 are functions which represent gross productivity and consumption, respectively, I is the ambient PAR(Photosynthesis Active Radiation) light intensity in the water column. $f_1 = aC[1 - \exp(-I/I_s)]$, $f_2 = \gamma C$, a is light-saturated specific growth constant, I_s is the light intensity of light saturation, and γ is

the specific loss constant proportional to a .

Results from the numerical simulations generally agreed with the observed distribution of phytoplankton productivity and biomass observed in estuaries with high concentrations of suspended sediments. From the simulation and the experiment, it was shown that although light increased the growth of phytoplankton, growth was sharply attenuated in the estuarine environment by the high concentration of living phytoplankton.

CSTT (Comprehensive Studies Task Team) model (Tett, 2003)

The CSTT model was originally developed by the UK's "Comprehensive Studies Task Team" to predict phytoplankton chlorophyll levels. This model is a steady-state simplification of a dynamic model that is applied to a horizontally and vertically uniform system or the upper water of a well-stratified system, that exchanges with the sea at a daily rate E determined by physical processes. A slight simplification of the model was used to simulate the steady-state response of chlorophyll, the limiting nutrient, and light availability to nutrient loading. In this model, both nitrogen and phosphorus are considered to be efficiently recycled within the microbial loop, and growth rate of plankton is controlled by the concentration of nutrient and light availability.

The key equations are:

$$\text{(chlorophyll)} \quad \frac{dX}{dt} = (\mu - L)X - E(X - X_0) - \frac{F}{V}X_0 \quad (1)$$

$$\text{(limiting nutrient)} \quad \frac{dS}{dt} = -\frac{\mu \cdot X}{q} + e\frac{L \cdot X}{q} - E(S - S_0) + \frac{S_i}{V}, \quad (2)$$

where the subscript 0 refers to the concentration of nutrient S or phytoplankton chlorophyll X in the sea and μ is phytoplankton growth rate (day^{-1}). L is

phytoplankton loss rate (day^{-1}) due to grazing by copepods or benthic animals, phytoplankton sinking, or disease, and e is the fraction of the nutrient element content of the lost material that is recycled. A key parameter q is the yield of chlorophyll from assimilated nutrient. s_i is the input of nutrient.

This model has been used to examine six sites including four fjords: Kongsfjorden (west coast of Spitzbergen); Gullmaren (Skagerrak coast of Sweden); Himmerfjorden (Baltic coast of Sweden); and the Firth of Clyde (west coast of Scotland), and two lagoons: Golfe de Fos (French Mediterranean); and Ria Formosa (Portuguese Algarve). The chlorophyll predictions for Kongsfjorden, Himmerfjorden and the inner Firth of Clyde are greater than the maximum chlorophyll observed during summer. In the case of the Ria Formosa, the observed maximum value is about twice the predicted maximum, but both predicted and observed maximum chlorophyll are low. Although CSTT is useful for distinguishing among eutrophic conditions, the simplicity of the current version of the CSTT model limits its use as a tool for diagnosing and predicting trophic status.

ASSETS (Assessment of Estuarine Trophic Status) model (Bricker, 2003)

Unlike the other models, ASSETS employs an integrated methodology. ASSETS was used to examine 138 estuaries in the continental United States in the United States National Estuarine Eutrophication Assessment (NEEA). ASSETS includes three diagnostic tools: a heuristic index of pressure (*Overall Human Influence, OHI*), a symptoms-based evaluation of state (*Overall Eutrophic Conditions, OEC*), and an indicator of management response (*Definition of Future Outlook, DFO*).

◦ *Pressure- OHI*

Human influences are classified into five grades: low, moderate low, moderate, moderate high, and high, according to the relative proportions ($m_h / (m_h + m_b)$) of

dissolved inorganic nitrogen (DIN) derived from anthropogenic and ocean sources.

where m_h is human-derived concentration, and m_b is background concentration.

For a well-mixed system:

$$\text{Human-derived concentration (} m_h \text{): } \frac{dM_h}{dt} = Qm_{in} - Qm_h - \frac{Qs_e}{\Delta s} m_h$$

$$\text{Background concentration (} m_b \text{): } \frac{dM_b}{dt} = -Qm_b - \frac{Qs_e m_b}{\Delta s} + \frac{Qs_e m_{sea}}{\Delta s}$$

where Q is the river flow (m^3s^{-1}), m_{in} is nitrogen concentration in the inflow (kg s^{-1}), m_{sea} is nitrogen concentration in the ocean (kg m^{-3}), and s_e is the mean estuarine salinity.

$$\text{When it reaches steady state, } \frac{dM_h}{dt} = 0 \text{ and } \frac{dM_b}{dt} = 0.$$

$$\text{Therefore, } m_h = \frac{m_{in}(s_o - s_e)}{s_o}, \quad m_b = \frac{m_{sea}s_e}{s_o}.$$

◦ *State- OEC*

Six parameters including primary symptoms (chlorophyll a, macroalgae and epiphytes) and secondary symptoms (dissolved oxygen, losses of submerged aquatic vegetation, and toxic algal blooms) of eutrophication are selected to express the overall eutrophic condition. Each symptom is defined by one of three possible states: high, moderate and low, expressed with numerical values (3, 2, 1). The area-weighted values of the six parameters for each zone are compared in a matrix to determine an overall ranking of eutrophic conditions for the estuary.

◦ *Response- DFO*

The response is based on an assessment of the susceptibility component of the system. Based on demographic projections, future nutrient pressure of a system can be characterized as decreased, unchanged, or increased.

Based on the assessments of OHI, OEC, and DFO for an estuary, an overall

classification grade is assigned: high, good, moderate, poor, or bad.

Part 3. Data Summary

NOAA identified six symptoms of eutrophication that are most directly related to nutrient inputs for classifying the eutrophic status of estuaries. Three of the six symptoms are considered as primary symptoms: algal abundance (using chlorophyll *a* as an indicator), epiphyte abundance, and macro-algae. These represent the first stages of water quality degradation associated with nutrient over-enrichment. These primary symptoms can lead to secondary symptoms: submerged aquatic vegetation loss, nuisance and toxic algal blooms, and low dissolved oxygen (Bricker, 1999). The model discussed here estimates the susceptibility of estuaries to various nitrogen loads by using predictions of chlorophyll *a* and dissolved oxygen.

Data on physical characteristics and nutrient loads are primary inputs for this modeling effort. Model output of chlorophyll and dissolved oxygen are compared to the category from the NOAA data set (Table 1). Data for volume, depth, water residence time, fresh water flow, and total nitrogen load (Table 1) were recompiled from the estuary database available on the National Estuarine Eutrophication Assessment (NEEA) website (<http://ian.umces.edu/index.html?http&&&ian.umces.edu/need/>). This data set was supplemented by additional data from National Oceanic and Atmospheric Administration (NOAA).

Table 1. Data Set for Homogeneous Estuaries

No.	Vertical Homogeneous Estuaries	Volume (m ³)	Depth (m)	Tau (day)	Total Nitrogen (kg N/day/km ³)	NOAA Chla*	NOAA DO**
1	Kennebec/Androscoggin Rivers	4.8E+08	6.27	10	71235.64	2	1
2	Casco Bay	5.1E+09	12.04	122	430.48	2	1
3	Great Bay	1.8E+08	3.78	31	12608.35	2	1
4	Hampton Harbor Estuary	2.6E+06	0.87	6	62604.31	2	1
5	Boston Harbor	1.2E+09	6.25	76	20423.63	2	2
6	Narragansett Bay	3.5E+09	8.31	109	5059.48	2	1
7	Gardiners Bay	3.3E+09	6.39	389	668.25	2	1
8	Connecticut River	9.3E+07	2.22	2	608828.01	2	1
9	Great South Bay	4.2E+08	1.1	199	30499.21	3	1
10	Hudson River/Raritan Bay	4.9E+09	6.13	45	43698.06	3	2
11	Barneгат Bay	1.2E+08	0.65	29	27559.37	3	1
12	Delaware Bay	1.3E+10	6.12	85	7478.43	2	1
13	Maryland Inland Bays	1.0E+08	1.92	126	6363.10	3	1
14	Chincoteague Bay	6.5E+08	1.94	158	339.95	2	1
15	Potomac River	6.5E+09	5.13	121	16259.15	3	3
16	Choptank River	1.3E+09	3.09	713	1244.32	2	1
17	Tangier/Pocomoke Sounds	3.5E+09	3.29	1118	851.49	3	1
18	Neuse River	1.3E+09	2.86	74	11646.61	3	1
19	Pamlico Sound	1.4E+10	2.93	959	79.44	2	1
20	Cape Fear River	2.5E+08	2.45	7	105988.26	3	1
21	Winyah Bay	4.5E+08	5.05	7	99848.06	2	2
22	St. Marys River/Cumberland Sd.	2.1E+08	3.34	29	13206.46	2	2
23	Biscayne Bay	8.6E+08	1.23	20	21366.73	1	1
24	Florida Bay	1.0E+09	0.62	272	751.45	2	3
25	South Ten Thousand Islands	1.4E+08	0.63	18	13624.87	2	3
26	North Ten Thousand Islands	2.8E+08	0.73	16	750.42	2	2
27	Rookery Bay	1.8E+07	0.5	43	1952.88	1	1
28	Charlotte Harbor	8.2E+08	1.63	59	6187.54	3	3
29	Sarasota Bay	2.7E+08	2.19	87	6864.45	2	2
30	Tampa Bay	2.7E+09	3	197	2267.92	3	1
31	East Mississippi Sound	1.5E+09	2.34	25	31329.36	2	2
32	Barataria Bay	3.6E+08	0.42	113	18650.72	3	2
33	Terrebonne/Timbalier Bays	8.6E+08	0.68	213	1631.40	3	1
34	Atchafalaya/Vermilion Bays	2.7E+09	1.2	3	503779.89	3	1
35	Sabine Lake	6.6E+08	2.49	10	97074.78	2	1
36	Brazos River	5.5E+07	4.62	3	1874913.52	2	2
37	San Antonio Bay	3.5E+08	0.59	30	95245.29	2	1
38	Corpus Christi Bay	1.5E+09	2.69	1320	3945.52	3	1
39	Upper Laguna Madre	2.0E+08	0.34	5	1353.37	3	2
40	Lower Laguna Madre	9.9E+08	0.76	233	25157.15	3	1
41	Monterey Bay	4.6E+10	83.75	3249	1050.42	2	1
42	Yaquina Bay	3.0E+07	2.13	13	95954.72	2	1
43	Hood Canal	2.7E+10	67.96	470	122.00	3	2

* 1: low eutrophication, <0.03 g N/m³; 2: medium eutrophication >0.03 & <0.12 g N/m³; 3: high

eutrophication >0.12 & < 0.37 g N/m³; 4: hyper eutrophication >0.37 g N/m³

** 1: low eutrophication >5 g O/m³; 2: medium eutrophication >2 & <5 g O/m³; 3: high

eutrophication <2 g O/m³

Most volume data are based on the best volume estimate from a digital bathymetric chart in cases for which they are available. Otherwise these data come from NOAA planimetry. Almost all of the depth data are from a digital bathymetric chart if available; otherwise they are also from NOAA planimetry. Water residence time was calculated using two different techniques: tidal exchange and tidal freshwater flush. Tidal exchange time is a salinity-based estimate of exchange, defined as: $(\text{Estimated Volume} / \text{net freshwater Volume per day}) * ((\text{coastal salinity} - \text{average salinity}) / \text{coastal salinity})$. Tidal freshwater flush time is based on NOAA calculations, using: $(\text{daily tide} + \text{freshwater volume}) / \text{system volume}$. We used the larger of the two as water residence time when they differed. Freshwater flow and total nitrogen load data are from NCPDI_1982-1991 (The National Coastal Pollutant Discharge Inventory).

The extent of stratification and eutrophication status data were extracted from the NOAA database for three conditions of stratification: Vertical Homogeneous (VH), Moderate Stratified (MS), and Highly Stratified (HS). Of these, only VH estuaries were used to test the model developed in this study. For a given estuary, if the stratification condition for high flow differs from that of low flow, the high flow condition was used.

Data for chlorophyll concentration have been difficult to acquire. Consistent data are not available from the STORET data management system of the Environmental Protection Agency (EPA), National Estuarine Research Reserve System (NERRS), or United States Geological Survey (USGS). Only a small amount of data could be obtained from published papers. Therefore, it was necessary to use the NOAA data set which is a compilation of survey data from aquatic science experts. In this data set only the category of eutrophic status was provided.

For the concentration of chlorophyll in the water, NOAA defines the breakpoints of 5, 20, and 60 $\mu\text{g Chl/l}$ as boundaries for Low, Medium, High, and Hyper eutrophic status respectively. Since the model, in this study, uses nitrogen (N) for all components, we converted those values to 0.03, 0.12, 0.37 $\mu\text{gN/l}$. These phytoplankton nitrogen break points were used to test the model. Similarly, for dissolved oxygen, the NOAA classification of Low, Medium, and High corresponds to breakpoints of 2 and 5 g/m^3 (Table 1).

Part 4. Model Structure

Phytoplankton depend on an average nitrogen-to-phosphorus (N: P) nutrient ratio of 16:1. If the ratio is greater than 16, phosphorus is the limiting factor. If the ratio is lower than 16, nitrogen will be the limiting factor. Although either phosphorous or nitrogen can limit phytoplankton growth, nitrogen is generally considered the most frequent driver of estuarine eutrophic conditions and currently is primarily the result of non-point sources (NSTC, 2003). Therefore, only nitrogen load is considered in this work.

As the model is a general one applied to all estuaries, values for physical characteristics, including light intensity and temperature, are uniform. Light was initially considered as a controlling factor for phytoplankton growth in the model. Under the average solar radiation, phytoplankton growth is limited by nitrogen concentration but light. Therefore, light limitation is not included here. The model is designed specially for the summer season, and because average temperature does not vary much, temperature is also not considered.

Estuarine biological responses to nitrogen loads can be controlled by the magnitude, frequency, and other characteristics of external drivers, but also by intrinsic characteristics of the estuaries. These intrinsic characteristics include both physical and chemical factors (depth, volume, salinity, water residence time, etc.) as well as biological factors (nature of ecological communities, organism categories, trophic interactions, etc.). However, to explore estuarine responses to key driving variables, a one-layer NPZ (nutrient-phytoplankton-zooplankton) model (Fig. 1) was developed for river-dominated, nutrient limited, well-mixed estuaries.

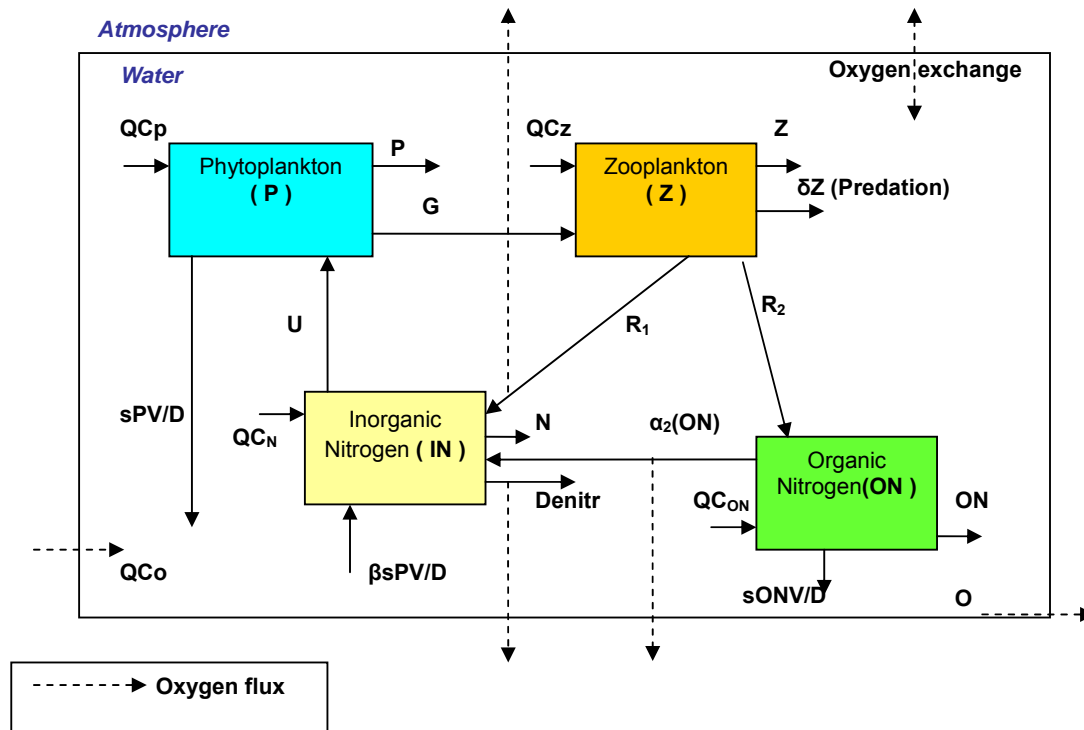


Fig. 1 Box-and-Arrow Flow Diagram for NPZ Model

In the NPZ model, nitrogen is composed of two forms: *IN* (inorganic nitrogen) and *ON* (organic nitrogen). The other three variables are *P* (phytoplankton), *Z* (zooplankton), and *O* (dissolved oxygen). Phytoplankton and zooplankton are modeled in their nitrogen equivalents. These variables are connected through a grazing term, predation, respiration, and sedimentation. Michaelis-Menten dynamics are used to simulate the nitrogen uptake by phytoplankton. As for the phytoplankton consumption by zooplankton, two terms are used here to make a comparison: linear grazing method and Michaelis-Menten grazing method. To simplify the model, zooplankton predation is calculated as a linear relationship.

Loading terms were modeled as an in-stream concentration times river flow, allowing the model to be written in terms of water residence time only. The load could then be varied by changing either the in-stream concentration or flow. Atmospheric

deposition on the water surface is not included because the area of the surface water is generally limited. However atmospheric deposition to the watersheds that reaches streams is included in the input of nitrogen to the estuary from terrestrial sources.

Phytoplankton growth is limited by nitrogen concentration:

$$\frac{dP}{dt} = \frac{QC_P}{V} - \frac{P}{\tau} + U - G - \frac{sP}{D} \quad (1)$$

where C_P is the concentration of the input of phytoplankton to the estuary (kg N /m³); Q is freshwater flow (m³/day); V is the volume (m³); $U = \frac{v_N N}{k_N + N} P$;

$G = \frac{v_P P}{k_P + P} Z$; N, P, Z (kg N/m³) are state variables which represent the concentration of inorganic nitrogen, phytoplankton, and zooplankton biomass, respectively; v_N, k_N and v_P, k_P are the Michaelis-Menten maximum growth rate (day⁻¹) and half-saturation constant (kg/day) for N uptake by phytoplankton and P grazing by zooplankton, respectively; D (m) is the average depth of the estuary; s is the sinking rate of P ; and τ is water residence time (day).

Zooplankton dynamics are modeled as:

$$\frac{dZ}{dt} = \frac{QC_Z}{V} - \frac{Z}{\tau} + G - R_1 - R_2 - \delta Z \quad (2)$$

where C_Z is the concentration of the input of zooplankton to the estuary (kg N /m³); $R_1 = \frac{\alpha_1 v_P P}{k_P + P} Z$; $R_2 = \frac{\alpha_2 v_P P}{k_P + P} Z$; and δ is fraction of zooplankton biomass loss

through predation.

Nitrogen recycling is proportional to zooplankton grazing because the phytoplankton are not completely grazed. A fraction of phytoplankton consumed by zooplankton are recycled back to the inorganic nitrogen pool (α_1) and the organic nitrogen pool (α_2). The remaining fraction ($1-\alpha_1-\alpha_2$) contributes to zooplankton

growth.

Equation related to inorganic N flux is shown below:

$$\frac{dN}{dt} = \frac{QC_N}{V} - \frac{N}{\tau} - U + R_1 + \alpha_2(ON) + \frac{\beta sP}{D} - Denitr \quad (3)$$

where C_N is the concentration of the input of nitrogen to the estuary from terrestrial source ($\text{kg N} / \text{m}^3$); $\alpha_2(ON) = \frac{\lambda_N \alpha_2 v_P P}{k_P + P} Z$; λ_N is the ON to N transfer rate;

and β is the fraction of settled phytoplankton that is recycled.

$Denitr$, representing denitrification, has been characterized by Nixon et al. (1996) in terms of the percent of terrestrial nitrogen load, ie:

$$100 \frac{Denitr}{I_N} = 20.8 \log(\tau_{mo}) + 22.4, \text{ where } \tau \text{ is residence time (years) defined as}$$

the ratio between estuarine volume and the freshwater flow through the estuary.

Or, $Denitr = I_N (0.208 \log(\tau) - 0.085)$, where τ is measured in days. This suggests that

the relationship between $Denitr$ and τ is valid only for $\tau > 2.6$ days.

The equation for organic nitrogen (ON) flux is:

$$\frac{dON}{dt} = \frac{QC_{ON}}{V} - \frac{ON}{\tau} + R_2 - \alpha_2(ON) - \frac{s'ON}{D} \quad (4)$$

where C_{ON} is the concentration of the input of organic nitrogen to the estuary ($\text{kg N} / \text{m}^3$), ON ($\text{kg N}/\text{m}^3$) are state variables which represent the concentration of organic nitrogen in an estuary, and s' is the sinking rate of ON .

Oxygen fluxes are also modeled. These fluxes include biological production and consumption, as well as the exchange between the surface water and atmosphere.

During photosynthesis, oxygen is produced when phytoplankton use the energy of the sun to convert carbon dioxide into carbohydrates. Oxygen is consumed during phytoplankton and zooplankton respiration. Oxygen is also consumed during the

decomposition of phytoplankton and zooplankton debris. In addition, benthic sediments also demand the dissolved oxygen (Garcia et al. 2002).

The equation related to oxygen fluxes is shown below:

$$\frac{dO}{dt} = \frac{QCo}{V} - \frac{O}{\tau} + \frac{Fo}{D} + \gamma U_1 - \gamma_1 R - \gamma_1 \alpha_2 (ON) - \frac{\gamma_2 O}{D} \quad (5)$$

where C_o is the concentration of the input of oxygen from terrestrial sources (kg O/ m³); O (kg/m³) represent the concentration of dissolved oxygen; γ and γ_1 are the oxygen to nitrogen ratio during photosynthesis and respiration; and γ_2 is the oxygen demand rate by benthic sediment.

F_o is the air-sea oxygen flux, g O₂/m²/day

$F_o = k * (O_{2s} - O)$, where k is diffusivity (m/d), O is the actual oxygen concentration, and O_{2s} is the oxygen saturation in the water.

Part 5. Model Results

Parameter values used by the model are based on literature values (Table 2). For the classification output, these same parameters are applied to all the estuaries because our main purpose is to examine the general eutrophication response to Tau and load. The data below represents the average condition for most estuaries.

Table 2. Parameter Values

Name	Units	Value	Description	Source
V	m ³	1.0E+09	Volume of estuary	Estimated for NOAA data set
τ	day	200	Residence time	Estimated for NOAA data set
D	m	5	Depth of estuary	Estimated for NOAA data set
C _N	kg N/m ³	0.002	input of N to the estuary	
C _P	kg N /m ³	0.0007	input of P to the estuary	
C _Z	kg N/m ³	0.0005	input of Z to the estuary	
C _{ON}	kg N/m ³	0.0005	input of ON to the estuary	
vn	day-1	2	Michaelis-Menten rate constant	Hopkinson and Vallino, 1995
kn	g N/m ³	0.03	MM half saturation const N	Hopkinson and Vallino, 1995
vp	day-1	1	MM rate constant	Hopkinson and Vallino, 1995
kp	g C/m ³	0.4	MM half saturation const	Hopkinson and Vallino, 1995
I ₀	daylight/da	29.200	Surface light intensity	Ryther, 1956
λ		0.115	Light extinction coefficient	Ryther, 1956
α_1		0.45	Fraction of grazing N recycling	
α_2		0.2	Fraction of grazing ON	
β		0.2	Fraction of benthic flux recycled	
s	m/day	0.01	Phyto sinking rate	
s'	m/day	0.5	ON sinking rate	
δ		0.1	1 st order zoo loss	
O _{2S}	g/m ³	9.5	Oxygen saturation in the water	
Y		2	O ₂ to N ratio	Scavia, 1980
Y ₁		9	O ₂ to ON ratio	
Y ₂		0.5	O ₂ exchange rate with sediment	
λ_{-N}		0.9	ON to N transfer ratio	
k	m/day	0.72	O ₂ exchange constant	Estimated from Stigebrandt,
icn	g N/m ³	0.20	initial condition N	
icp	g N/m ³	0.10	initial condition P	
icz	g N/m ³	0.10	initial condition Z	
icon	g N/m ³	0.05	initial condition ON	
ino	g O/m ³	9	O ₂ concentration in water	

A simulator in Visual Basic for Applications (VBA), the macro-language of Microsoft Excel, was written to solve the model. Equations use a modified 4th-order

Runge-Kutta integration routine (cf Press et al.1992). Simulations can be run in two modes:

1. “non-steady state”- in which a single simulation proceeds for a specified time interval.
2. “steady state”- in which multiple runs are made over a range of both water residence time and N load, holding all other parameters constant, until either a “steady state” has been reached, or the simulation reaches its end time.

Effects of changing parameters

Most modeled cases reached steady state (e.g. Fig. 2, Fig. 3). Steady state is an ideal state that is not always realized in a real environment because of complex dynamics and changing driving factors. However, use of steady state simulations is helpful for the analysis. In these simulations, phytoplankton biomass increases rapidly while nutrients are consumed initially. After the phytoplankton peak, they decrease due to nutrient limitation and zooplankton grazing, eventually reaching steady state. Zooplankton develop a profile similar to that of phytoplankton with a time lag in reaching a steady state.

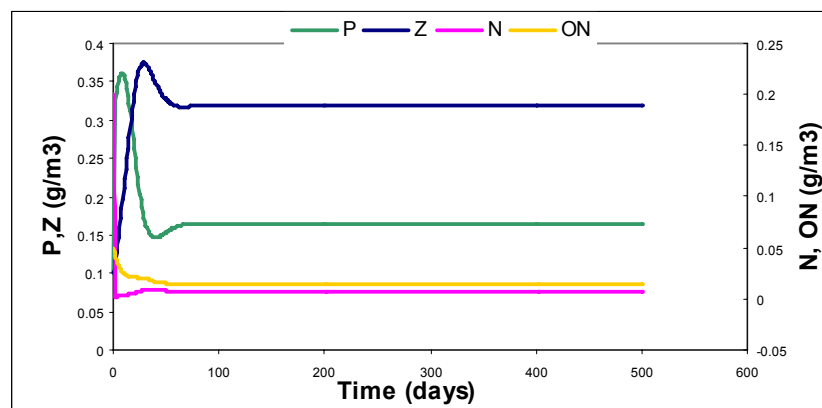


Fig. 2 Changes of variables according to time

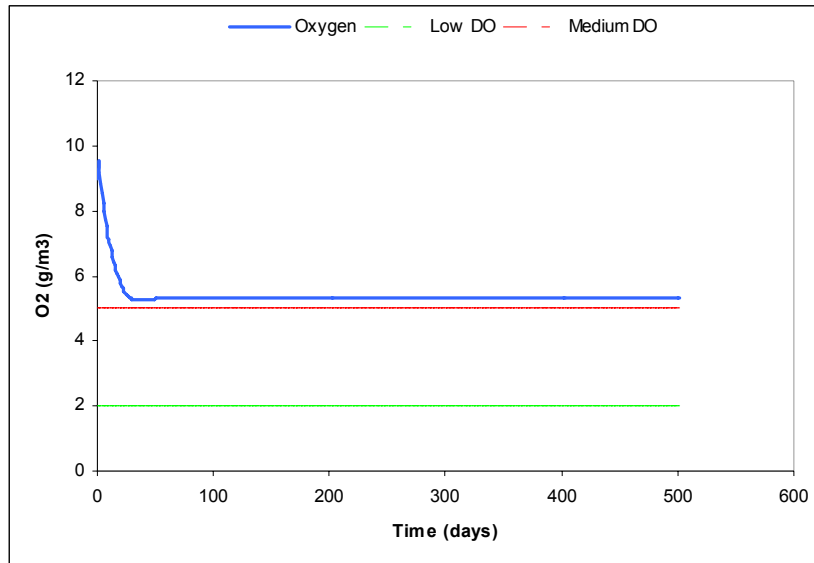


Fig. 3 Changes of oxygen concentration according to time

Changing parameters alters the model dynamics, and may result in oscillatory or other time-varying behaviors. Fig. 4 illustrates the typical steady state response of phytoplankton. Fig. 5 shows the effect of increasing the nitrogen concentration in riverine load from 2 to 14 mg N/l, resulting in oscillations around the intermediate value. Fig. 6 reveals the effect of changing estuary volume from 10^9 to 5×10^8 m³, indicating susceptibility differs greatly, depending on specific estuarine physical characteristics compared to Fig. 2.

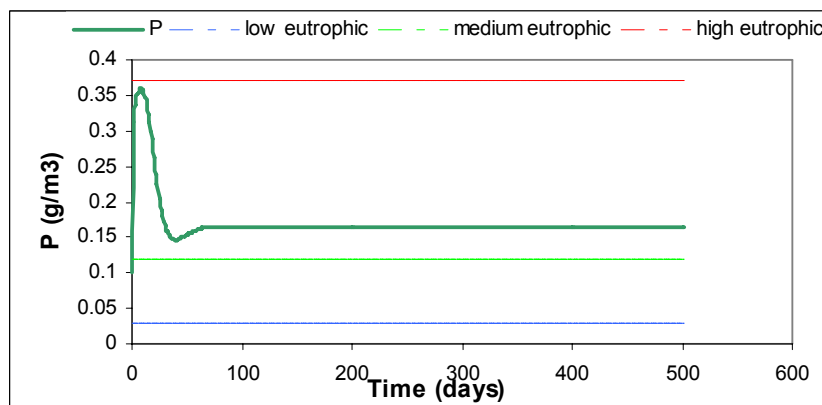


Fig. 4 Response of phytoplankton to steady input of nitrogen

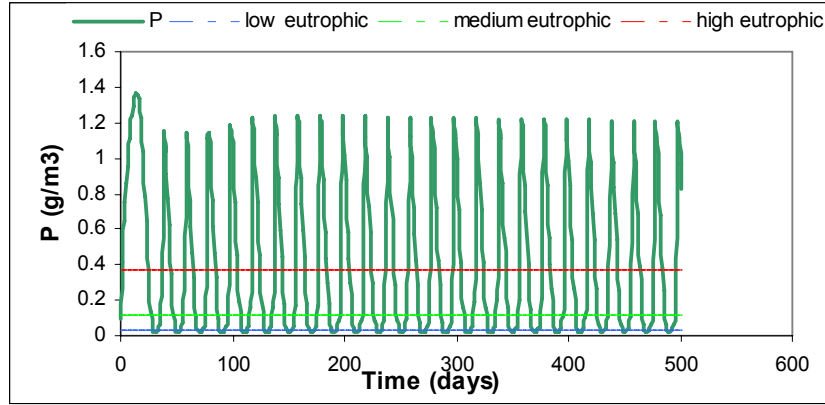


Fig. 5 Oscillation response of phytoplankton

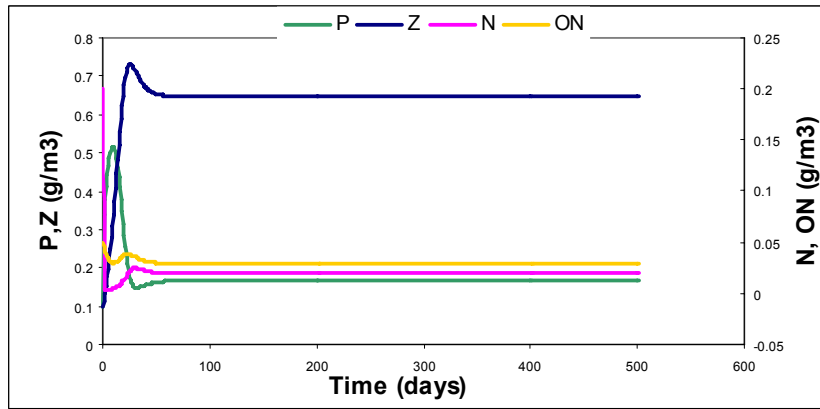


Fig. 6 Effects of changing volume on response to nitrogen load

Two methods of zooplankton grazing on phytoplankton were simulated here. The results by the linear grazing method (Fig. 7) and Michaelis-Menten method (Fig. 8) produced different results. While the phytoplankton and zooplankton concentrations are significantly different, inorganic nitrogen and organic nitrogen concentration are similar in both cases. The phytoplankton concentration in steady state under the Michaelis-Menten grazing term is comparatively lower than that under the linear grazing term. Alternatively, the zooplankton concentration under the Michaelis-Menten mechanism is higher than that under the linear mechanism.

The denitrification process does not affect the dynamics of the four variables, but

does affect their final concentrations (Fig. 9, Fig. 10).

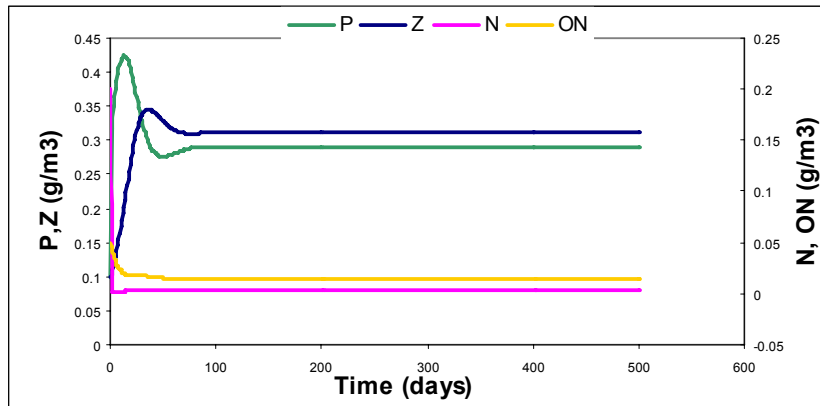


Fig. 7 Liner method of zooplankton grazing on phytoplankton

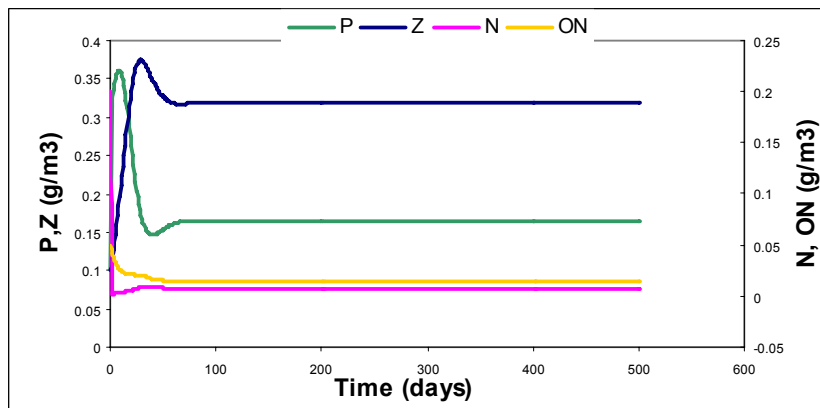


Fig. 8 Michaelis-Menten method of zooplankton grazing on phytoplankton

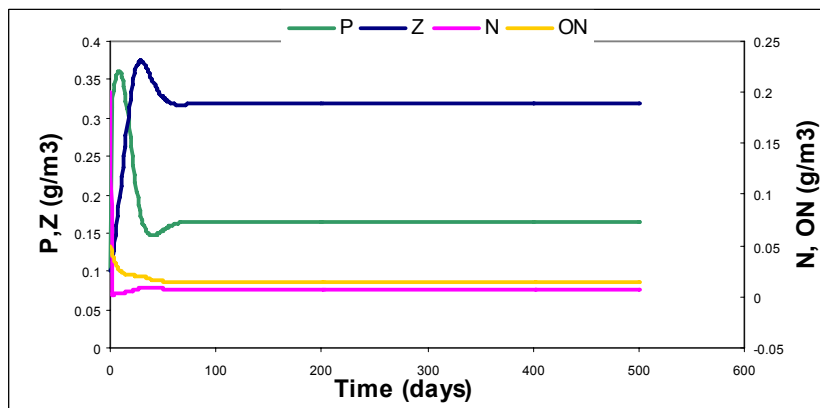


Fig. 9 Response without denitrification process

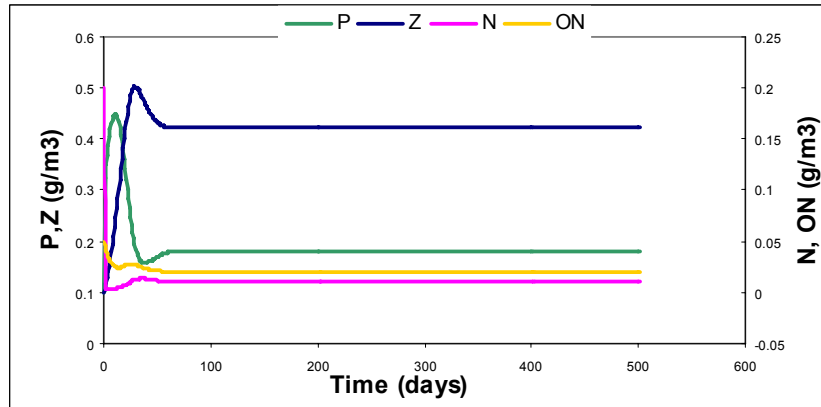


Fig. 10 Response with denitrification process

Effects of residence time and nutrient loads

At different volumes and freshwater flow rates, the model calculates steady-state values of nitrogen, phytoplankton, zooplankton, and dissolved oxygen as a function of nitrogen loads. From these results, we can determine the eutrophic conditions (phytoplankton and oxygen concentrations) at combinations of Tau and nitrogen load.

Fig. 11 reveals phytoplankton response as a function of Tau under five random-chosen nutrient loads: 200, 6598, 59912, 123890 and 190000 kg N/day/m³. For the same Tau, phytoplankton biomass increases as load increases. The phytoplankton response graph suggests that phytoplankton response is almost linear with logical values of residence time initially, and then either plateaus for lower loads or decreases and then plateaus for higher loads.

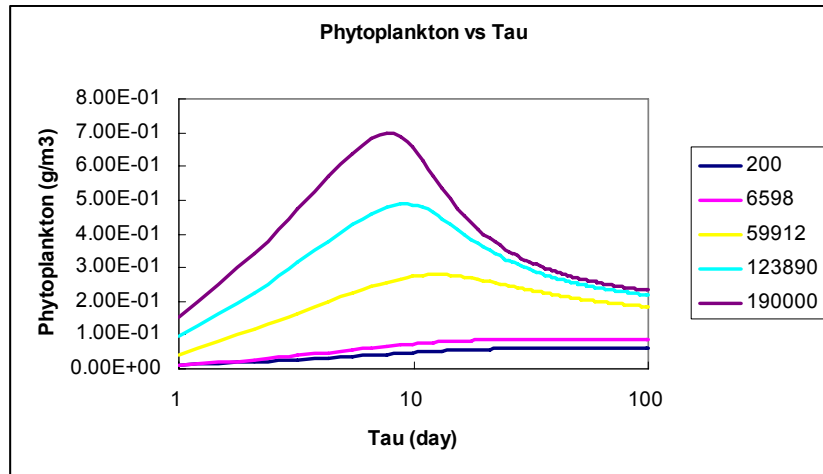


Fig. 11 Phytoplankton vs Tau under different loads

Fig. 12 shows dissolved oxygen response as a function of Tau under the same five nutrient loads. Dissolved oxygen concentration increases as load increases when Tau is smaller than 10 days, while it decreases as load increases then Tau is bigger than 10 days. For lower loads, dissolved oxygen concentration increases almost linearly with residence time at first, and then plateaus. Estuaries with lower loads are usually oligotrophic water bodies. If Tau is larger, more algae could stay longer in the estuary, then produce more oxygen through photosynthesis. Therefore, dissolved oxygen concentration is high. For higher loads, the concentration increases linearly first, and then decreases, and plateaus. Estuaries with higher loads are usually somewhat eutrophic water bodies. Although more algae could stay longer and produce more oxygen through photosynthesis, depletion of dissolved oxygen by respiration and decomposition is more. Thus, the dissolved oxygen concentration is low.

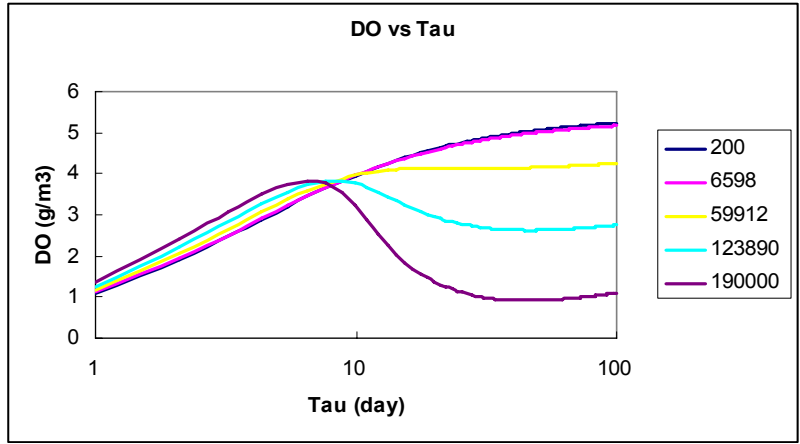


Fig. 12 Dissolved Oxygen vs Tau under different loads

Fig. 13 shows the same results, but as a function of loading for a range of Tau. Among the given six residence time scenarios with values of 1, 11, 31, 61, and 100 days, the residence time of 11 produces the highest phytoplankton-biomass, with residence time equal 1 resulting in the lowest. Phytoplankton biomass increases with Tau more under lower loads than those under higher loads. For residence times of 31, 61 and 100 days, the phytoplankton responses are quite similar. The results show that the phytoplankton response varies remarkably over residence time. In this model, the phytoplankton biomass is maximized at residence time of around 11 days.

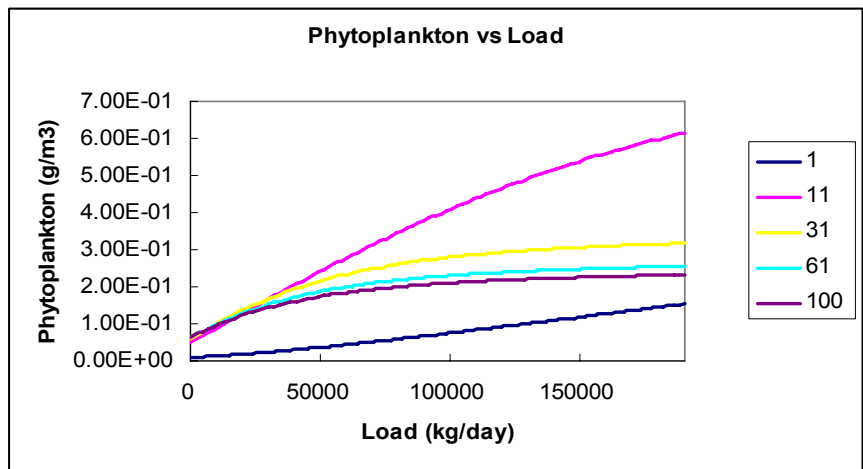


Fig. 13 Phytoplankton vs load under different Tau's

Fig. 14 indicates dissolved oxygen concentration response to loads. The responses

are almost the same under the residence time of 31, 61, and 100 days. Dissolved oxygen increases only under residence time of 1 day and decreases for other residence time.

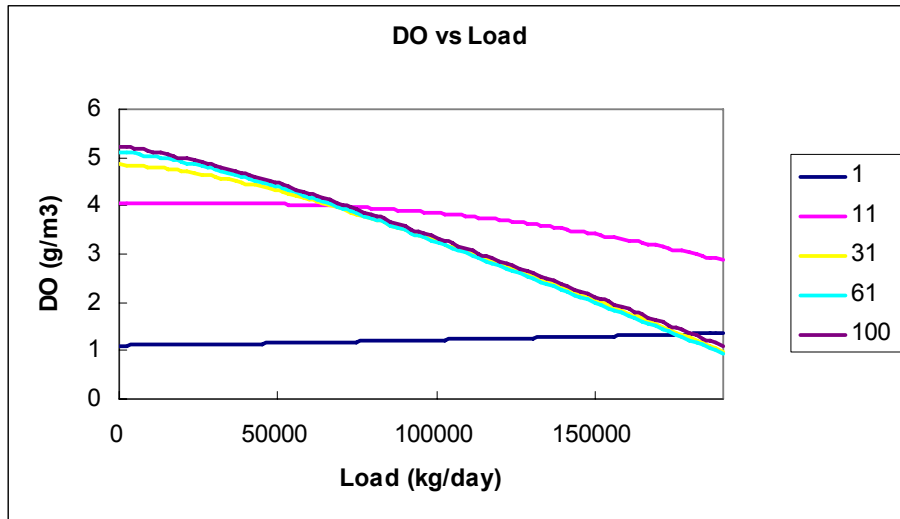


Fig. 14 Dissolved Oxygen vs Load under different Tau's

General classification

Model results can also be expressed as a response surface in load and Tau (Fig. 15). For a given Tau, the phytoplankton response increases with increasing load. However, for a given load, the phytoplankton response increases and then decreases with increasing Tau. The model also suggests that when load is low enough, no matter how long the residence time, phytoplankton biomass is always very low. If residence time is short enough, the phytoplankton biomass is also very low even if the nitrogen load is very high. The highest value appears in the high load area where Tau is about ten days.

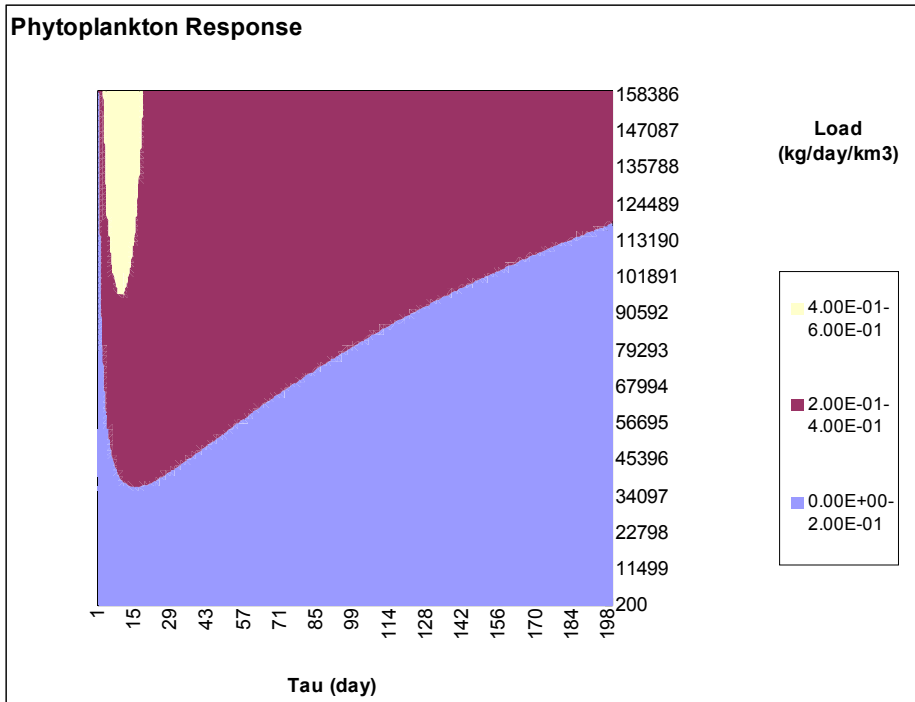


Fig. 15 Surface graph of phytoplankton response to loads and Tau's

When Tau is very low, DO is controlled by Tau; DO increases as Tau increases.

When Tau's is larger, DO concentration is controlled by load; DO decreases with increasing load. The lowest DO concentration occurs when load is extremely high.

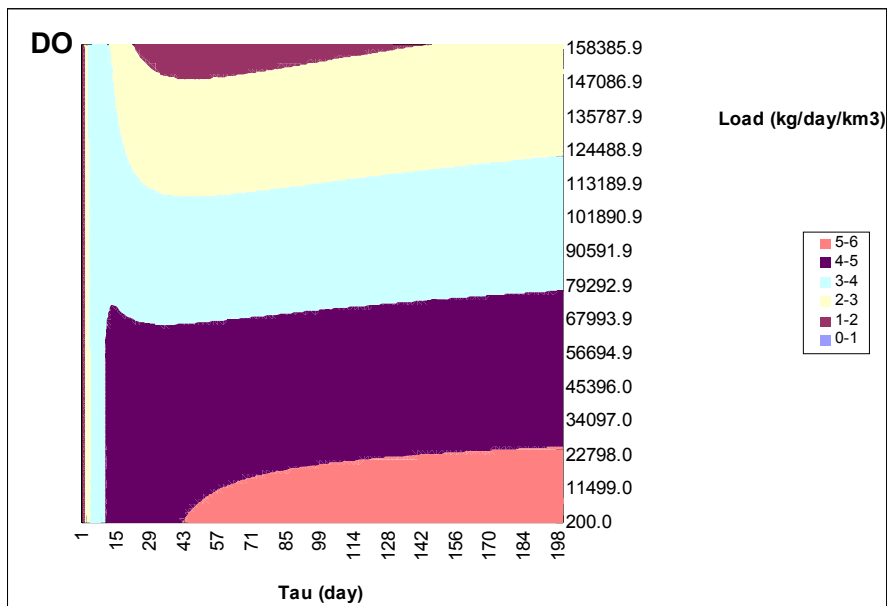


Fig. 16 Surface graph of Dissolved Oxygen response to loads and Tau's

These results can be compared to estuarine observations. If load and Tau are known for a specific estuary, the observed phytoplankton and dissolved oxygen concentration represent the system response. Fig. 17 and Fig. 18 represent phytoplankton response and dissolved oxygen comparisons between NOAA eutrophication categories and the NPZ model output. The colored areas represent the different categories of eutrophic status from the NPZ model. The points with different colors represent corresponding categories for estuaries from the NOAA data set. Data from approximate forty-five well-mixed estuaries were available for comparison; only sixteen of those estuaries fall within the model predictions.

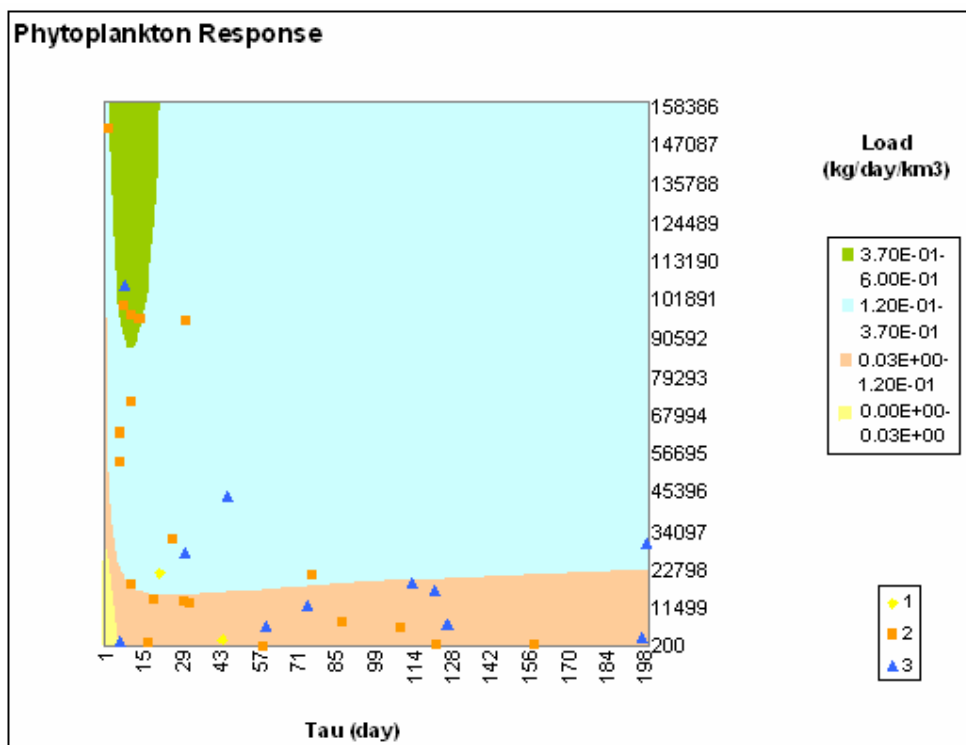


Fig. 17 Comparison of NOAA data with NPZ model output

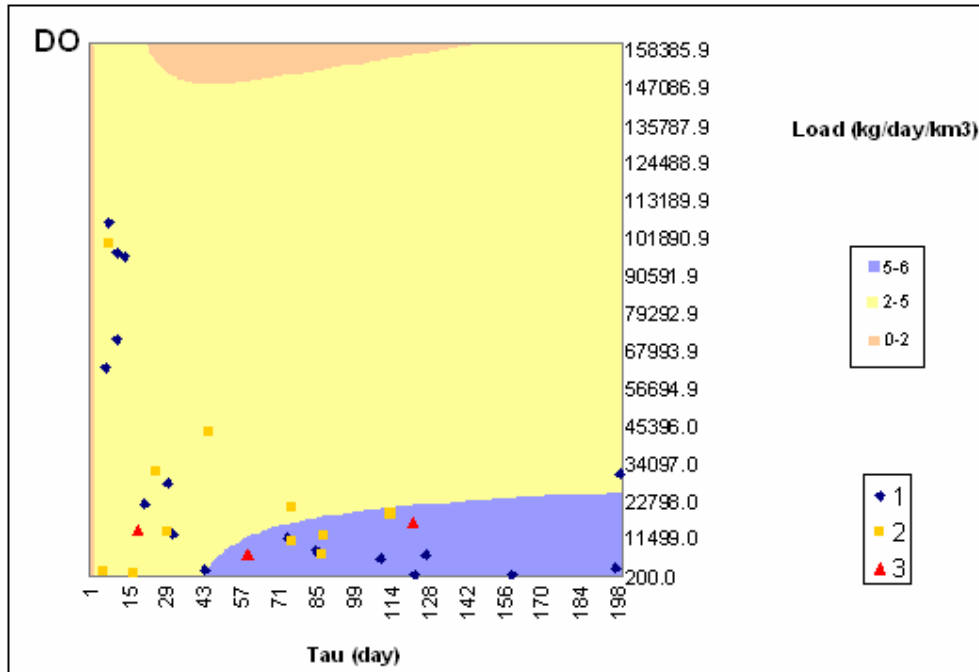


Fig. 18 Comparison of NOAA data with NPZ model output

Part 6. Conclusion and discussion

In an attempt to classify eutrophic condition of estuaries, five mass balance equations are developed for phytoplankton, zooplankton, inorganic nitrogen, organic nitrogen and oxygen. The model shows different responses to nutrient loads and water residence time. According to the different responses, estuaries were generally classified as low, medium, high, and hyper eutrophication.

Some reasonable and interesting results were produced. For example, phytoplankton response to residence time has the same trend under different loads; higher load produces more phytoplankton biomass. Given the five Tau scenarios, phytoplankton biomass under Tau of 41.4 is the highest, and the one under 1.0 is the lowest.

After comparing the model results with the NOAA data set, some estuaries did match the predictions, while others did not. This may be because some estuaries are light limited, phosphorus limited or even silica limited, however, this model only works for the nutrient-limited ones. First of all, in the general model, the values of the volume data, depth data and other estuarine characteristic data are the average values. Therefore, the output probably does not fit for the estuaries with extreme values. Second, eutrophic states from the NOAA data set represent the yearly condition, while the results from the model represent the states in summer. Third, the stratification situation in the data set needs further examination.

Compared to site-specific estuarine models, the model developed here is much simpler, and with further development, could be a useful screening tool for the management of estuaries. Some physical factors such as light, temperature, and wind could be added to make it a more complex model. It may also be appropriate to expand the model into two layers. Other nutrients such as phosphorous and silica

could also be added. At present, the model is designed for summer steady state conditions. The effects of seasonality could be explored more fully in future investigations.

The NPZ model still has a place in estuarine classification. A variety of behaviors including various steady state and regular oscillations may serve as a basis for caution in developing a classification of coastal ecosystems.

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