

# Modeling Atmosphere-Ocean Interactions and Primary Productivity

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The strength of our food chain, regardless of the number of its links, must be dependent on that first fundamental link which joins it organically to the inorganic elements of which all living forms are composed, elements which are unavailable until woven into living tissue on the mysterious loom of the chlorophyll-bearing plant. And this, in the entire aquatic world, is par excellence the diatoms.

Mann 1921

## In this chapter you will:

- Be exposed to relations between atmosphere-ocean interactions and primary productivity;
- Be sensitized to the importance of iron in the marine geochemistry and its central role in the physiology of marine primary producers; and
- Learn how to use stoichiometric equations within a STELLA model, and how to trace chemical elements—much like the **cohorts** of a **population**—through different stages.

## 7.1. Introduction

The heat budget, and hence the climate of the Earth, is sensitive to changes in the atmospheric greenhouse gas composition. Next to water vapor, carbon dioxide ( $\text{CO}_2$ ) is the most important atmospheric greenhouse gas affecting the Earth's radiative balance. Greenhouse gases raise the mean temperature of the Earth by absorbing and trapping long-wave radiation from the planet surface that would otherwise be lost to space.

Global warming is a phrase that has become extremely popular in both media and environmental circles since it was discovered that, beginning with the Industrial Revolution of the 19<sup>th</sup> century, anthropogenic fossil fuel use has increased atmospheric ( $\text{CO}_2$ ) from 280 to 360 ppm and warmed the Earth by approximately  $0.4^\circ\text{C}$ . Changes in atmospheric  $\text{CO}_2$  concentrations affect, and are affected by, interactions between the atmosphere and ocean, with potentially far-reaching implications for marine and terrestrial life. Understanding the effect of increased  $\text{CO}_2$  on climate, biogeochemical cycles,

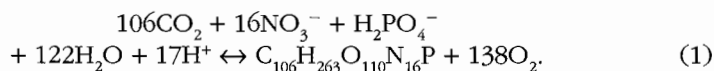
ocean and terrestrial plant productivity has become the focus of much scientific research.

The purpose of this chapter is to demonstrate the relations between the atmosphere-ocean CO<sub>2</sub> system and marine primary productivity as it is regulated by the supply of two essential nutrients: nitrogen (most importantly in the form of nitrate, NO<sub>3</sub><sup>-</sup>) and iron (Fe). The model developed in this chapter draws on concepts from many aspects of oceanography. It is based on fundamental concepts in equilibrium chemistry (the carbonate system), biology and ecology (nutrient kinetics and primary production). The model is heuristic and not a quantitative estimate of the impacts of anthropogenic CO<sub>2</sub> increases and Fe limitation on primary productivity. Rather, the model's primary purpose is to demonstrate the coupling between **partial pressure** of CO<sub>2</sub> [pCO<sub>2</sub>] in the atmosphere, ocean chemistry and biology, and to explore changes in atmospheric [pCO<sub>2</sub>].

## 7.2. Greenhouse Gases and Climate

Our current understanding of the ocean-atmosphere system and how anthropogenic activities will affect future climate changes relies heavily on our understanding of past perturbations of global climate detected in the geological record. Measurements of CO<sub>2</sub> concentrations in air bubbles trapped in polar ice cores have demonstrated that atmospheric CO<sub>2</sub> fluctuations of approximately 80 ppm (Petit et al. 1999) accompanied temperature fluctuations during the most recent Quaternary glacial-interglacial transition (12,000 years ago) on a time scale of 10<sup>3</sup>–10<sup>4</sup> years. Whether present increases in atmospheric CO<sub>2</sub> will result in similarly drastic changes in global climate requires greater knowledge to what degree the ocean, the largest reservoir of inorganic carbon, will act to buffer atmospheric increases.

Because the vast majority of the combined atmosphere-ocean inorganic carbon pool resides in the subsurface ocean (Sarmiento & Orr 1991), fluctuations in atmospheric CO<sub>2</sub> concentrations and the resulting shifts in global climate are thought to be forced by changes in the oceanic carbon cycle (Sundquist & Broecker 1985). Today, surface ocean CO<sub>2</sub> concentrations are in equilibrium with the atmosphere, while the deep ocean contains more CO<sub>2</sub> than could result from air-sea gas exchange alone (Broecker, Peng & Engh 1980). The surplus of CO<sub>2</sub> in the deep ocean is maintained by a mechanism referred to as the **biological pump** (Sarmiento & Bender 1994). The biological pump sequesters CO<sub>2</sub> from the atmosphere through the reduction of CO<sub>2</sub> by photoautotrophic organisms. In surface waters of the oceans, these organisms fix inorganic carbon (along with other nutrients) into organic molecules according to the equation for **photosynthesis**:



A fraction of the reduced carbon is removed from communication with the atmosphere when it sinks out of surface waters under the influence of gravity, and is remineralized in the deep ocean. The stoichiometry of the reaction represents, on average, the composition of the sinking biogenic material. Ratios of the major inorganic nutrients in the ocean interior are set by the net result of the redox reaction of carbon fixation and remineralization.

The constant stoichiometry of marine export production, often called the **Redfield ratio**, is used to estimate carbon fluxes from changes in surface-water nutrient concentrations (Redfield et al. 1963). In the modern ocean, the yield of this generalized reaction is thought to be limited by the supply of N (in the form of  $\text{NO}_3^-$ ) to the euphotic zone because upwelled N-to-nutrient ratios are on average below the Redfield values (Anderson & Sarmiento 1994; Falkowski 1997). Although the specific causes for variations in atmospheric  $\text{CO}_2$  on glacial-interglacial time scales remain unknown, one way to explain the glacial increase of the oceanic carbon inventory and resulting reduction of atmospheric  $\text{CO}_2$  levels is through increased biological pumping of carbon (increased export production) to the deep ocean (Martin 1990).

### 7.3. High-Nutrient, Low-Chlorophyll (HNLC) Regions

In certain areas of today's ocean, such as the Southern Ocean and the Equatorial Pacific, the presence of excess surface nutrients and the virtual absence of phytoplankton biomass imply that the biological pump is not operating to its full potential (Martin 1990). These areas are referred to as high nutrient-low chlorophyll (HNLC) regions. A portion of the decrease in glacial atmospheric  $\text{CO}_2$  could be accounted for if the biological pump were able to draw down these excess nutrients and associated inorganic carbon from the HNLC. In fact, organic carbon preserved in the sediments indicates that export production from HNLC surface waters has covaried with atmospheric  $\text{CO}_2$  levels during the Quaternary (Berger et al. 1989). One way to increase the efficiency of the biological pump (export production) would be to enhance local levels of primary production.

The iron hypothesis was advanced in order to address why and how productivity in HNLC regions could have increased so remarkably during the last glaciation. Martin (1990) proposed that the reduction of atmospheric  $\text{CO}_2$  during the past glaciation event was caused by increased biological production due to greater aeolian supply of Fe to ocean surface water. During the last glaciation, Fe fluxes to the ocean surface were approximately 50 times higher than present-day fluxes, and there is good correspondence between the supply of Fe and atmospheric  $\text{CO}_2$  inferred from ice-core records (Petit et al. 1999). The hypothesis assumes that in certain HNLC areas of the present-day ocean, photosynthetic fixation of in-

organic carbon is limited by low ambient Fe concentrations. Another assumption is that increased aeolian Fe supply could relax this limitation and allow excess surface nutrients to be utilized. Evidence supporting both of these assumptions comes from recent laboratory and large scale field experiments (Coale et al. 1996b; Martin et al. 1994; Martin et al. 1989; Morel, Rueter & Price 1991b; Sunda & Huntsman 1997). Iron's importance in the marine geochemistry of C and N stems from its central role in the physiology of marine primary producers.

Iron is an essential element for all living organisms (Williams 1981). Photoautotrophic physiology requires Fe for the production of chlorophyll, cytochromes and for the fixation and metabolism of nitrogen as a component of specific metalloenzymes. Although Fe is required in trace quantities compared with other major mineral nutrients, it is largely insoluble in oxygenated seawater. Surface-water concentrations of soluble, biologically available Fe are exceedingly low ( $< 1 \times 10^{-9}$  mol L<sup>-1</sup>) in the open ocean and depth profiles resemble those of other major plant nutrients (Bruland 1983; Martin & Gordon 1988; Martin et al. 1989). The transport of Fe into the **euphotic zone** as estimated from simple advective/diffusive models alone appears to be insufficient to allow marine **phototrophs** to deplete ambient **macronutrients** such as nitrate and phosphate (Martin 1990). Without additional sources of Fe, such as **aeolian deposition**, HNLC regions appear to be Fe-limited ecosystems with low levels of phytoplankton biomass, primary productivity and export production.

## 7.4. Atmosphere-Ocean Interaction Model

The model is a one-dimensional, time-dependent box model that tracks the movement of carbon, nitrogen (NO<sub>3</sub><sup>-</sup>), and Fe through a conceptualized open-ocean ecosystem. With the exception of NO<sub>3</sub><sup>-</sup>, nutrients are permitted to cycle through four major reservoirs: the atmosphere, the surface ocean, the deep ocean and the sediment. We assume that atmospheric inorganic nitrogen deposition is insignificant compared with the flux of upwelled nitrogen to the surface ocean reservoir. Vertical particulate fluxes from the surface to deep ocean in the model result from the sinking of phytoplankton cells (primarily diatoms and calcite-forming organisms).

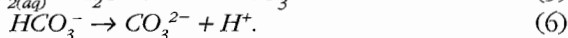
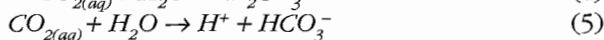
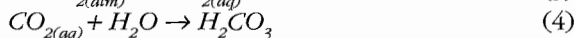
Before we discuss the structure and function of the model, it is important to explain the biological and chemical processes that form the heart of the model equations. Keeping track of the various currencies in the model—C, N and Fe—is made simple using STELLA and a PC. However, important concepts in carbonate chemistry and nutrient kinetics underlie the task of accounting for fluxes of C, N, and Fe, and the chemical changes they undergo. Clearly understanding the following principles will make applying and interpreting the model easier.

### 7.4.1. Inorganic Carbon Fluxes

When the processes of photosynthesis and respiration are balanced in the biosphere the concentration of atmospheric  $\text{CO}_2$  is regulated by equilibration with the ocean surface water  $[\text{pCO}_2]$ . Equilibrium between atmosphere and surface water  $[\text{CO}_2]$  is achieved through the exchange of carbon dioxide across the air-sea interface and is governed by the difference in partial pressure between the atmosphere and ocean surface waters and the piston velocity ( $\tau$ )—a measure of the diffusivity of  $\text{CO}_2$  and surface water mixing:

$$(\text{Air-sea exchange} = \tau (p\text{CO}_{2(\text{atm})} - p\text{CO}_{2(\text{aq})}). \quad (2)$$

Although changes in the concentration of  $\text{CO}_{2(\text{atm})}$  are relatively easy to model, the concentration of  $\text{CO}_{2(\text{aq})}$  is a function of the carbonate chemistry of seawater. The solubility of  $\text{CO}_2$  in seawater exceeds that for other inert gases because it can exist as three distinct species, according to the following thermodynamic relations:



The sum of these dissolved inorganic carbon species is designated  $C_t$  and is defined as

$$C_t = \text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}. \quad (7)$$

In order to solve for any of the inorganic carbon species, two of the following four parameters must be known:  $\text{pH}$ ,  $C_t$ ,  $p\text{CO}_{2(\text{aq})}$  and  $\text{TA}$  (total alkalinity).  $\text{TA}$  is defined as the sum of all the bases that can accept a proton at the  $\text{H}_2\text{CO}_3$  endpoint:

$$\text{TA} = \text{HCO}_3^- + 2(\text{CO}_3^{2-}) + \text{B}(\text{OH})_4^- + \text{OH} - \text{H}^+ + \text{other bases}. \quad (8)$$

When characterizing the system in terms of  $\text{CO}_2$  alone, alkalinity can be simplified to the total carbonate alkalinity ( $\text{CA}$ ):

$$\text{CA} = \text{HCO}_3^- + 2(\text{CO}_3^{2-}). \quad (9)$$

Before the concentration of  $\text{CO}_{2(\text{aq})}$  can be known, we must calculate the  $\text{pH}$  ( $\text{pH} = -\log [\text{H}^+]$ ) of the system. In order to limit the complexity of the calculations, we assume that in the  $\text{pH}$  range 7.8–8.5 the relation is a linear function of  $C_t$ :

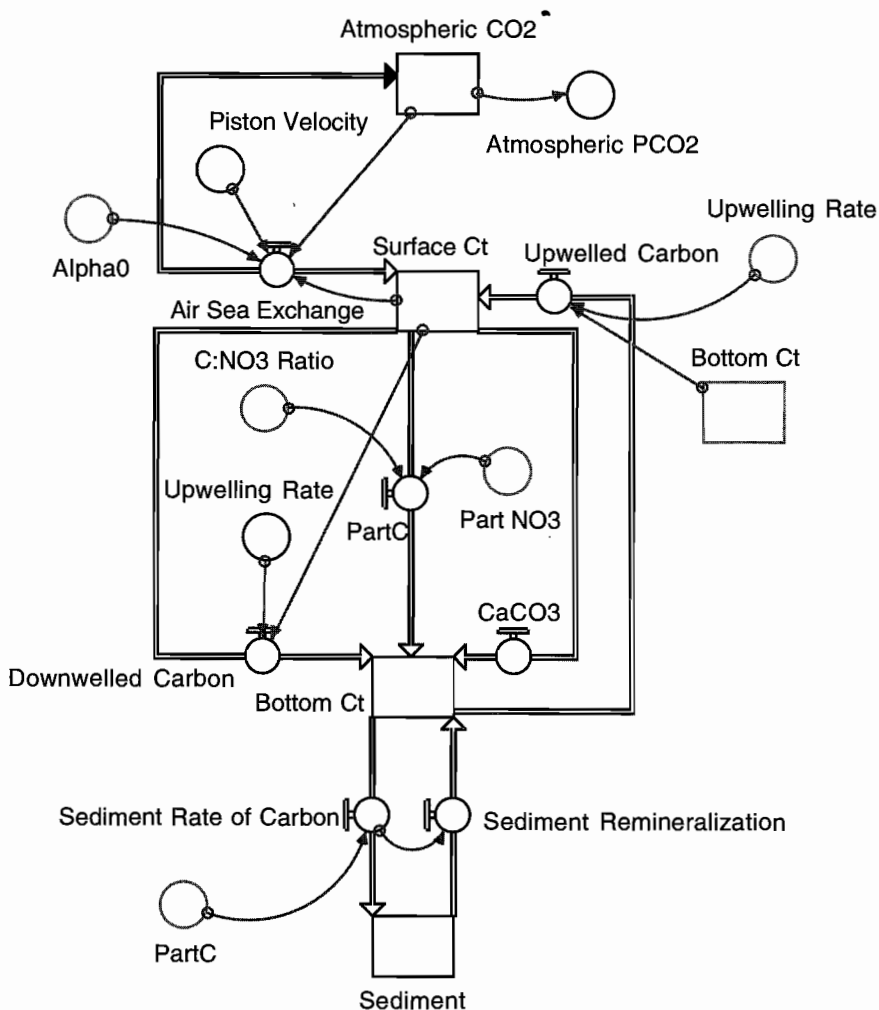


FIGURE 7.1

$$pH = -1805.4 \cdot C_t + 12.1. \quad (10)$$

Having solved for  $pH$  given  $C_t$  and  $CA$ , we can now calculate the concentration of  $CO_{2(aq)}$  using the ionization fractionation parameter ( $\alpha_o$ ) and the relation

$$CO_{2(aq)} = C_t \alpha_o \quad (11)$$

where

$$\alpha_o = (1 + 10^{-6.3}[H^+]^{-1} + 10^{-16.6}[H^+]^{-2})^{-1}. \quad (12)$$

Solving equation (2) at each time step enables us to determine the flux of  $\text{CO}_2$  from the atmosphere into the ocean (and in the reverse direction if the sign is negative). The concentration of  $\text{CO}_2$  in a given volume of atmosphere (ppm/v) can easily be calculated from the total molar amount of  $\text{CO}_2$ . The corresponding calculations are carried out in the  $\text{CO}_2$  module shown in Figure 7.1. In that module, the particulate C associated with sinking N is calculated using the average C/N ratio of marine plankton of  $6.6 \text{ mol mol}^{-1}$  (Redfield et al. 1963). Diffusion of  $\text{CO}_2$  into and out of the surface ocean from and to the atmosphere is set by the concentration gradient of  $\text{CO}_2$  between the atmosphere and the ocean. Calculations of surface  $p\text{CO}_2$  and  $\text{pH}$  are shown in Figure 7.2. Note that in the real world  $\alpha_0$  is also a function of temperature and the ionic strength of seawater.

#### 7.4.2. Nutrient Regulation of Phytoplankton Carbon Fixation

The growth and sinking of marine phytoplankton represents an important conduit through which atmospheric  $\text{CO}_2$  can enter, and be sequestered in, the deep ocean. The growth of marine phytoplankton requires the presence of many nutrients. Recent laboratory and field studies have shown N and Fe to be particularly important (Coale et al. 1996b; Price et al. 1994). Nitrogen in the form of ammonium is an essential component of amino acids, the building blocks of proteins. Nitrogen limitation therefore results in a host of problems at biochemical and biophysical levels, causing reduced  $\text{CO}_2$  fixation and ultimately reduced growth. In the oxygenated modern ocean, the thermodynamically stable form of N is nitrate ( $\text{NO}_3^-$ ). Before nitrate can be incorporated into amino acids, for example, it must be reduced to  $\text{NH}_3^-$ . This incorporation is accomplished with the two iron-containing enzymes, nitrite and nitrate reductase.

Iron is an essential part of the photosynthetic apparatus. Iron limitation leads to a decrease in the efficiency of light energy conversion to reducing agents (Greene et al. 1991; Greene et al. 1992). In areas of the ocean with high  $\text{NO}_3^-$  concentrations but low chlorophyll and low productivity, an addition of iron stimulates uptake of  $\text{NO}_3^-$  by marine phytoplankton,

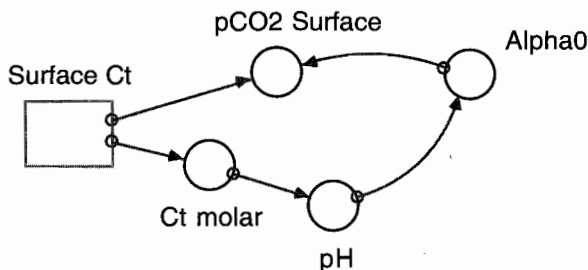


FIGURE 7.2

which is accompanied by a draw-down of atmospheric  $p\text{CO}_2$  (Cooper et al. 1996).

Uptake of nitrate after addition of iron can be approximated (Coale et al. 1996) by a simple Michaelis-Menten function of uptake velocity ( $V_{\text{NO}_3^-}$ ) as a function of substrate concentration (Fe), the maximum uptake velocity ( $V_{\text{max}}$ ) and the concentration of Fe supporting half saturated uptake ( $K_s$ ) where  $V_{\text{NO}_3^-} = 1/2 V_{\text{max}}$ :

$$V_{\text{NO}_3} = (V_{\text{max}} N [\text{Fe}]) / (K_s + [\text{Fe}]). \quad (13)$$

Equation (13) is used in Figure 7.3, to calculate  $\text{NO}_3^-$  uptake, or the conversion of dissolved inorganic N to particulate N that is then removed to deep water.  $K_s$  is set to 5pM and  $V_{\text{max}}$  N to .11 mol per year.

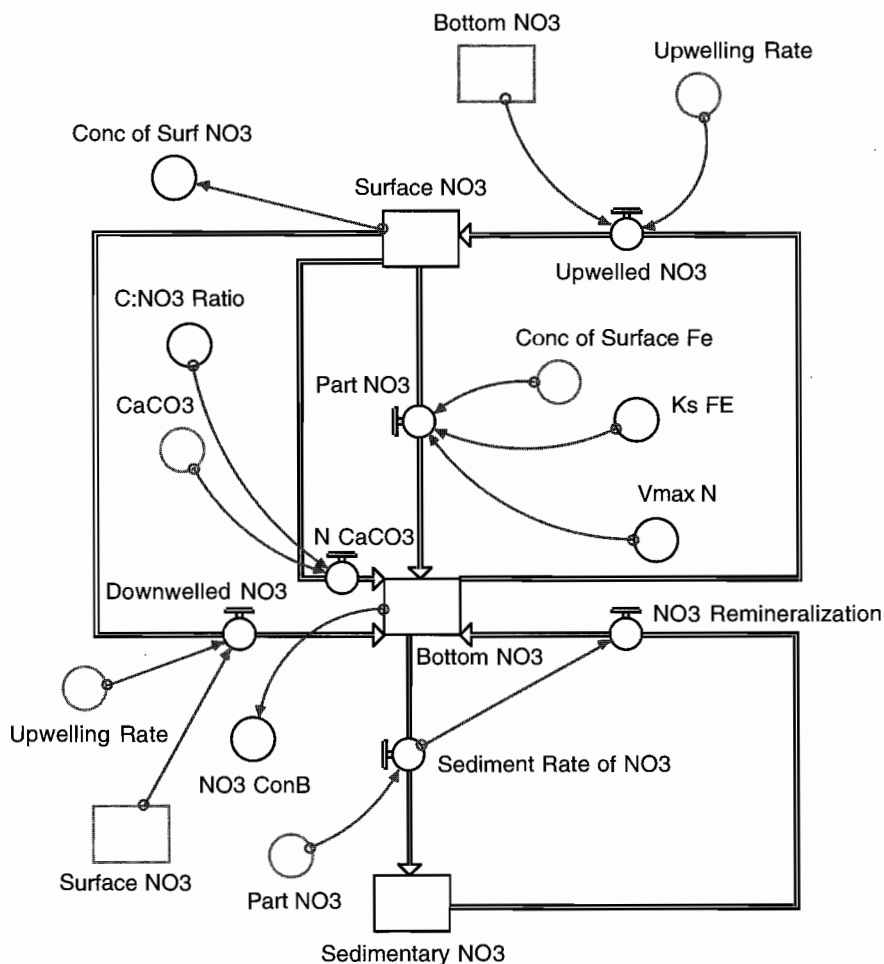


FIGURE 7.3



The structure of the Fe module of this model follows that of the N and C modules and is shown in Figure 7.4. Analogous to Figure 7.3, this module uses the Michaelis-Menten function to calculate particulate Fe fluxes to the deep ocean, using an average Fe : N ratio. The value for the Fe : N ratio applied in the model ( $1.65 \times 10^{-4}$  mol mol<sup>-1</sup>) has been determined for species of marine phytoplankton maintained in laboratory culture (Morel & Hudson 1984).

In the model, the major particulate flux of carbon from the surface water to the deep ocean and sediments occurs in the form of CaCO<sub>3</sub> burial. We incorporate in the model a constant background flux (i.e. independent of Fe availability) of C, N and Fe from calcite-forming organisms (Broecker & Peng 1982). Calculating downward particulate flux of C, N, and Fe in this manner assumes that:

- (a) ocean nutrient inventories remain constant;
- (b) the downward flux of particulate material results largely from the growth and sinking of **diatoms** (Goldman 1993);
- (c) the relative elemental ratios of C : N : Fe in sinking biogenic material are constant over the time scales considered in the model;
- (d) the downward flux of biogenic material or export production in this model is set by the input of Fe into the surface ocean;
- (e) when Fe concentrations are sufficient for maximum NO<sub>3</sub><sup>-</sup> uptake the downward flux of particulate C and, therefore, atmospheric CO<sub>2</sub> concentrations are controlled by, and equal to, the upwelling flux of NO<sub>3</sub><sup>-</sup> from deep water to the surface ocean. This is also the definition of new production (Dugdale & Goering 1967; Eppley & Peterson 1979).

Additionally, the model assumes that:

- (f) downwelling and upwelling fluxes of the dissolved chemical species are calculated based on the concentration of the species (mol) and the mean ocean downwelling and upwelling rates of 0.39 m (day)<sup>-1</sup> (Broecker & Peng 1982);
- (g) particulate matter burial equals 1% of the flux of the particulate matter to the deep ocean;
- (h) particulate matter remineralization occurs on the time scale of ocean mixing ~3000 years (Broecker & Peng 1982). This implies that on these time scales there is no organic matter preservation (i.e. steady-state).

Assumptions (a)–(h) link the C, N and Fe portions of the model. Despite a fixed relation between the incorporation of C, N and Fe into particulate matter the relative drawdown of carbon from the atmosphere and surface ocean into the deep ocean is a function of the concentrations of the two major plant nutrients N and Fe. Changing either the ratio of C : N : Fe in particulate matter or the absolute uptake of N (mol yr<sup>-1</sup>) does not alter the model's function—it will only change the relative drawdown or accumulation of CO<sub>2</sub> in the atmosphere and surface ocean. Fluxes of dissolved C, N

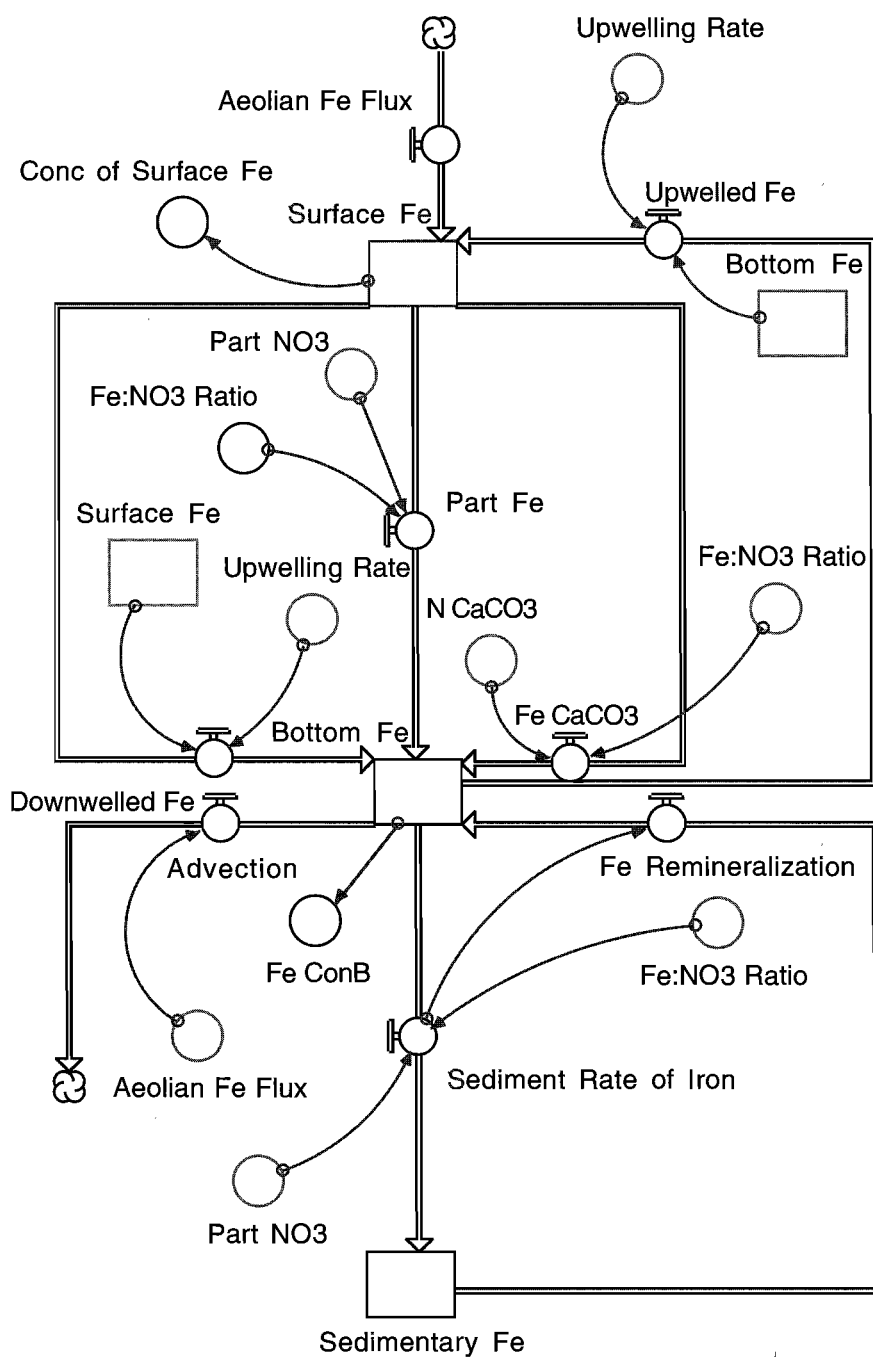


FIGURE 7.4

and Fe in and out of the surface and bottom waters are a function of the concentration gradient of the nutrient and the velocity of the flux (measured in  $\text{m day}^{-1}$ ). Because of deep-ocean remineralization of particulate matter, the concentration of C, N and Fe is higher in the deep ocean than at the surface. This results in a positive flux of nutrients into the surface water. Changes in ocean circulation patterns occurring over geologic time scales more than likely alter the magnitude of this flux (Boyle 1988).

## 7.5. Model Results and Discussion

To run the model, we initialize it with data for nutrient concentrations and atmospheric  $\text{CO}_2$  that reflect modern levels. We assume an initial  $\text{CO}_2$  concentration of the atmosphere of  $10.9 \mu\text{M m}^{-3}$ , and  $[\text{pCO}_2]$  of the atmosphere of  $345 \mu\text{atm}$ . We set  $C_t$  for surface and bottom water to  $2.19 \text{ mM}$  ( $= 219 \text{ mol}/100 \text{ m}^{-3}$ ) and  $2.31 \text{ mM}$  ( $= 7854 \text{ mol}/3400 \text{ m}^{-3}$ ), respectively. Initial  $[\text{Fe}]$  in surface and bottom waters are set at  $0.26 \text{ pM}$  ( $= 2.6 \cdot 10^{-8} \text{ mol}/100 \text{ m}^{-3}$ ) and  $1.2 \text{ pM}$  ( $= 4.08 \cdot 10^{-8} \text{ mol}/3400 \text{ m}^{-3}$ ), respectively. Initial  $\text{NO}_3^-$  concentrations in surface and bottom waters are  $12.0 \mu\text{M}$  ( $= 1.2 \text{ mol}/100 \text{ m}^{-3}$ ) and  $30 \mu\text{M}$  ( $= 102 \text{ mol}/3400 \text{ m}^{-3}$ ).

The results of the first scenario are derived for an aeolian Fe flux of  $2.048835 \cdot 10^{-7} \text{ mol}/100\text{m}^{-3}$  per year and are shown as Graph 1 in Figures 7.5 and 7.6. In these figure are also plotted the results of model runs that assume, respectively, a two-fold (Graph 2), four-fold (Graph 3), eight-fold (Graph 4) and sixteen-fold (Graph 5) increase in the aeolian flux of Fe.

Graph 1 in Figures 7.5 and 7.6 assumes that in HNLC regions primary productivity, and the amount of  $\text{CO}_2$  that can be removed from the atmosphere, are set by the combined Fe fluxes from upwelling and aeolian deposition. An increase in the total flux of Fe into the surface waters (Graphs 2–5 in Figures 7.5 and 7.6) will change the complex chemistry of iron in seawater. Phytoplankton are thought to only access the free ion of Fe for growth (Hudson & Morel 1993; Morel, Rueter & Price 1991; Sunda 1994). The free-ion concentration of Fe in solution is a function of the solubility, degree of complexation by organic ligands, absorption/scavenging and photo-reduction/oxidation reactions in the surface and deep ocean (Johnson, Gordon & Coale 1997). Therefore, a realistic model of iron/nitrate interactions should include a component that calculates the various pools of iron, both bioavailable and refractory. On longer time scales considered in this model, we assume that the free-ion activity of Fe is a linear, increasing function of total Fe in the system, so that any increase of ambient Fe will lead to an increase in production. Increasing the complexity of the model with respect to Fe speciation does not change its qualitative behavior.

Because HNLC regions are far removed from terrestrial sources of Fe and continental-shelf sediments, riverine Fe fluxes and advective Fe inputs to surface waters are extremely low. Therefore, the primary inputs of Fe required

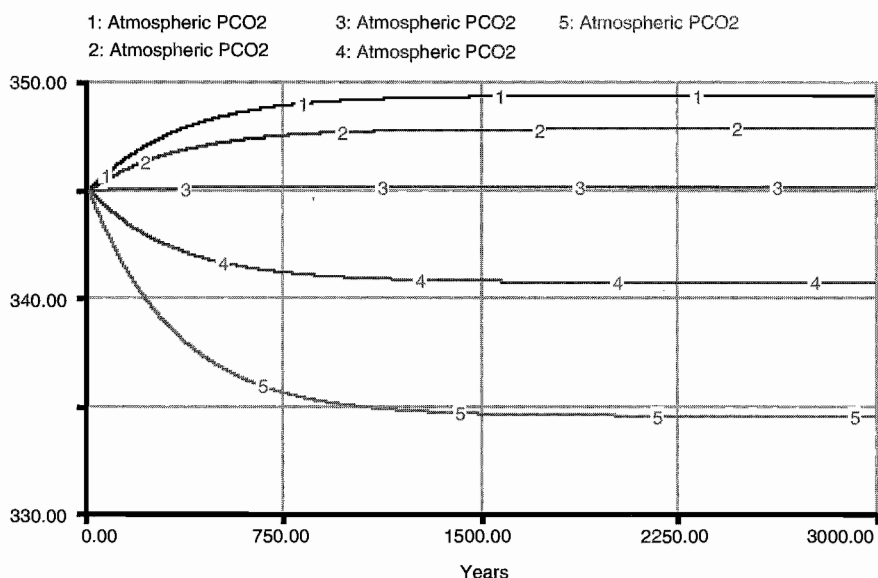


FIGURE 7.5

to promote photosynthesis in these ecosystems must come from either upwelled water, or the aeolian flux (Coale et al. 1996a; Martin 1990). As mentioned above, Fe is extremely insoluble in oxygenated seawater resulting in very low amounts of bioavailable Fe (available for uptake by phytoplankton). In fact, bioavailable Fe in HNLC regions is below the best estimates of  $K_s$  (where Fe uptake is half saturated) for marine diatoms. This suggests that Fe uptake may be diffusion limited for all but the smallest phytoplankton (Hudson & Morel 1993).

Figure 7.5 shows that higher aeolian Fe fluxes reduce the steady-state levels of atmospheric  $[pCO_2]$ , with a four-fold increase resulting in same long-run  $[pCO_2]$  that is nearly the same as the initial conditions. Figure 7.6 shows the temporary downward adjustments in Surface  $C_i$  and ultimate rise to the steady-state level that accompany initially high levels in Surface Fe. The exception is the case in which there is a sixteen-fold increase in Fe, and a continuous reduction of Surface  $C_i$ .

A simplification of the model is that the size structure of the phytoplankton community is not considered, which can have important implications for the biogeochemical cycling of carbon and the productivity of the ecosystem. A defining feature of HNLC regions is the absence of large phytoplankton ( $>5 \mu m$ ) and the predominance of small primary producers (Chavez 1989; Price et al. 1994). However, upon relief of iron limitation (and the diffusion barrier), larger diatoms can rapidly dominate the biomass of primary producers (Price et al. 1994; Price et al. 1991). This shift in the

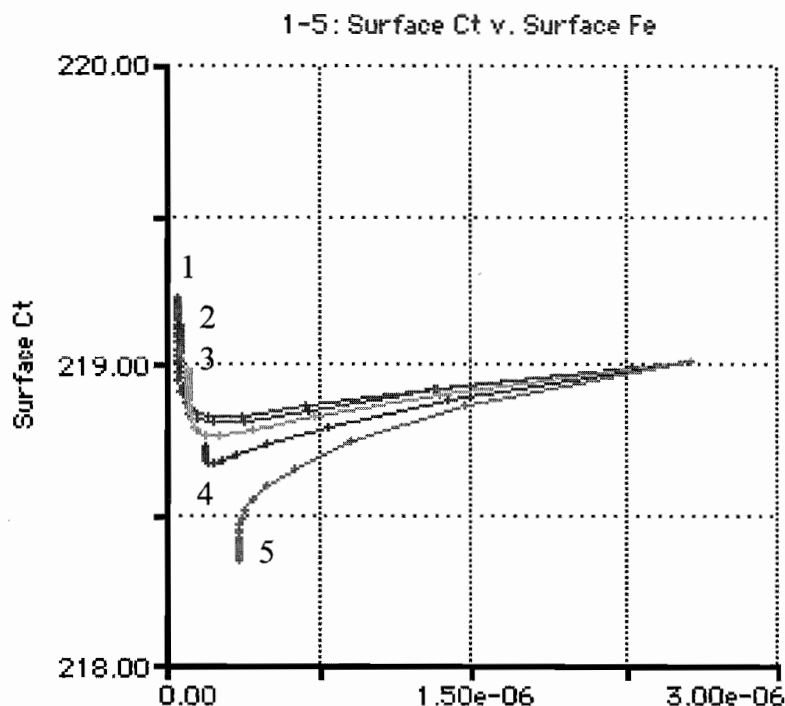


FIGURE 7.6

size of primary producers affects both the kinetics of nutrient uptake—largely through changes in the surface-area-to-volume ratio (Morel et al. 1991a)—and the amount of export production from the ecosystem (removal of  $\text{CO}_2$  from surface to deep water).

A constant relation is assumed between surface water  $[\text{Fe}]$  and uptake rate of  $\text{NO}_3^-$  in the model that is characteristic of large, rapidly growing phytoplankton. In HNLC regions, where Fe concentrations are limiting, small cells predominate which have lower  $K_s$ ,  $V_{\max\text{NO}_3^-}$ , and absolute growth rates than larger diatoms. Under Fe-limiting conditions, the phytoplankton community is unable to remove all upwelled  $\text{NO}_3^-$  and a surplus is observed to exist in surface waters. Each unutilized mole of  $\text{NO}_3^-$  represents 6.6 moles of potential atmospheric  $\text{CO}_2$  drawdown if the biological pump were operating efficiently. When Fe is added to the system large phytoplankton proliferate and deplete  $\text{NO}_3^-$  with a concomitant drawdown of atmospheric  $\text{CO}_2$ . Because the model underestimates the utilization of nutrients (C and N) under Fe-limiting conditions, the difference in atmospheric  $\text{CO}_2$  concentrations between Fe deplete and replete scenarios is a conservative estimate.

Over the geologic time scales of the model, the simplification to a homogenous population of phytoplankton still enables us to represent this

system. The model shows that under the initial conditions the supply of  $\text{NO}_3^-/\text{Fe}$  to the surface ocean is significantly higher compared with the Redfield ratios of particulate matter, indicating iron limitation (Figure 7.5). The amount of Fe input to the surface can only support a downward flux of particulate carbon that equals 5% of the potential given  $\text{NO}_3^-$  inputs. Under these conditions the ocean is a source of  $\text{CO}_2$  to the atmosphere. This phenomenon is typical of warm water upwelling systems where high- $Cl$ , nutrient-rich bottom water reaches the surface, is warmed, decreasing the solubility of  $\text{CO}_2$  in water, and diffuses into the atmosphere (Cooper et al. 1996).

## 7.6. Conclusions

This model represents physical processes very simply: heat exchange is not represented, mixing rates are constant, and in the one-dimensional model no lateral advection occurs. The temperature of surface waters has a profound effect on the solubility of  $\text{CO}_2$  and the resulting equilibrium concentration of dissolved  $\text{CO}_2$  (Millero 1995). Because cold water holds much more  $\text{CO}_2$ , the high-latitude HNLC regions (Subarctic Pacific and Southern Ocean) are more likely to act as sinks for atmospheric  $\text{CO}_2$  despite inefficient surface-nutrient utilization. In addition, the Southern Ocean is an important area of deepwater formation where cold surface waters and inorganic and organic carbon effectively and rapidly communicate with the ocean interior. Regionally specific models that incorporate temperature-dependent equilibrium constants for the carbonate system may allow for more accurate calculation of  $\text{CO}_2$  fluxes. We expect that the equilibrium constants used for this model (20°C) lead to a conservative estimate of air-sea  $\text{CO}_2$  exchange. Including cold surface waters with increased production in response to Fe additions should lead to a much greater effect on the atmospheric  $p\text{CO}_2$ .

Other simplifications in this model that would otherwise contribute to the remineralization of nutrients and export flux in marine ecosystems are the exclusion of higher trophic-level grazers and the microbial loop. These trophic levels effect the recycling of nutrients in surface waters, and therefore the amount of export production. However, we assume that the overall production in oligotrophic waters (and hence, the maximal drawdown of  $\text{CO}_2$ ) is regulated by the upwelling flux of  $\text{NO}_3^-$  and, more importantly in the HNLC, the combined upwelling and aeolian inputs of Fe. Therefore, the effects of these annual and inter-annual processes are minimal compared with the *a priori* knowledge of iron limitation in this system.

Because this model is in **steady-state**, the sources and sink terms are constant; on geologic time scales, this is not true. The model could be easily

modified to incorporate changes in the  $\text{NO}_3^-$  inventory driven by Fe availability by adding a sink and source term sensitive to surface Fe concentrations. Increasing the Fe flux to surface water has the potential to effect the relative rates of nitrogen fixation and denitrification. These interactions have been hypothesized to regulate the oceanic inventory of oxidized nitrogen on geologic time scales (Falkowski 1997). In essence, an increase in Fe and the concomitant increase in nitrogen fixation would have the eventual effect of increasing the upwelling concentration of  $\text{NO}_3^-$  in the world's oceans. This creates another potential positive feedback between iron supply and primary production. If, on the other hand, the relative ratio of nitrogen fixation/denitrification decreases,  $\text{NO}_3^-$  is consumed and the maximum potential for primary production decreases.

The parameterizations of the model simplify the complexity of some smaller-scale chemical and ecological processes, and limit the model's applicability over large temporal and spatial scales. As a consequence, the model only *approximates* the dynamics of the atmosphere-ocean carbon cycle and the biogeochemical behavior of N and Fe in an oligotrophic marine ecosystem on geologic time scales (10,000–100,000). The model may serve as a tool for understanding the ocean carbon cycle and its effect on regulating atmospheric  $p\text{CO}_2$ . The model demonstrates in simple form the regulation of carbon sequestration to the deep ocean by  $\text{NO}_3^-$  and Fe, and shows alternative  $p\text{CO}_2$  changes in response to changes in the Fe flux.

## 7.7. Questions and Tasks

- Without changing the model, predict what would happen to our planet under the following conditions:
  - 100x decrease in the solubility of  $\text{CO}_2$  in water;
  - No deep-ocean mixing with the surface layer;
  - No effect of Fe on rate of incorporation of N into organic matter;
  - 100x increase in  $V_{\text{max}} \text{NO}_3^-$ .

Now, introduce these changes into the model and see whether your predictions agree with the results.

- How is the chemistry of  $\text{CO}_2$  in seawater different from that of  $\text{O}_2$ ? Why is that important for the ocean's ability to sequester inorganic carbon from the atmosphere?
- What would happen to the  $\text{CO}_2$  in the ocean and atmosphere if there was a:
  - 1 pH unit decrease in the seawater?
  - 1 pH unit increase in the seawater?
- If a new organism invaded the ocean and had a C : N ratio of 1000, how would this affect the global carbon cycle?

## ATMOSPHERE-OCEAN INTERACTION MODEL

Calculation of pCO<sub>2</sub> in Surface Waters

$\text{Alpha0} = 1 / (1 + (1.28825\text{E-}06 / (10^{-\text{pH}})) + (9.77237\text{E-}16 / ((10^{-\text{pH}})^2)))$

$\text{Alpha1} = ((\text{pH} / 10^{-6.3}) + 1 + (10^{-10.3} / \text{pH}))^{-1}$

$\text{Alpha2} = (((\text{pH})^2 / 10^{-16.6}) + (\text{pH} / 10^{-10.3}) + 1)^{-1}$

$\text{Ct\_molar} = \text{Surface\_Ct} / 1\text{e}5$

$\text{pCO2\_Surface} = (\text{Surface\_Ct} / 1\text{e}5 * \text{Alpha0} / 3.16\text{e-}2) * 1\text{e}6$

$\text{pH} = -1805.4 * \text{Ct\_molar} + 12.1$

CO<sub>2</sub> Module

$\text{Atmospheric\_CO2}(t) = \text{Atmospheric\_CO2}(t-\text{dt}) + (-\text{Air\_Sea\_Exchange}) * \text{dt}$

INIT Atmospheric\_CO2 = 10.9

OUTFLOWS:

$\text{Air\_Sea\_Exchange} =$

$\text{Piston\_Velocity} * ((\text{Atmospheric\_CO2} / 1\text{e}6) - ((\text{Surface\_Ct} / 1\text{e}5) * \text{Alpha0}))$

$\text{Bottom\_Ct}(t) = \text{Bottom\_Ct}(t-\text{dt}) + (\text{Downwelled\_Carbon} + \text{PartC}$

$+ \text{Sediment\_Remineralization} + \text{CaCO3-}$

$\text{Upwelled\_Carbon-}$

$\text{Sediment\_Rate\_of\_Carbon}) * \text{dt}$

INIT Bottom\_Ct = 7854

INFLOWS:

$\text{Downwelled\_Carbon} = (\text{Surface\_Ct} / 100) * \text{Upwelling\_Rate}$

$\text{PartC} = (\text{Part\_NO3} * \text{C:NO3\_Ratio})$

$\text{Sediment\_Remineralization} =$

$\text{Delay}(\text{Sediment\_Rate\_of\_Carbon}, 2, 0)$

$\text{CaCO3} = 15$

OUTFLOWS:

$\text{Upwelled\_Carbon} = (\text{Bottom\_Ct} / 3400) * \text{Upwelling\_Rate}$

$\text{Sediment\_Rate\_of\_Carbon} = \text{PartC} * .01$

$\text{Sediment}(t) = \text{Sediment}(t-\text{dt}) +$

$(\text{Sediment\_Rate\_of\_Carbon-}$

$\text{Sediment\_Remineralization}) * \text{dt}$

INIT Sediment = 0.44

INFLOWS:

$\text{Sediment\_Rate\_of\_Carbon} = \text{PartC} * .01$



OUTFLOWS:

Sediment\_Remineralization =

Delay(Sediment\_Rate\_of\_Carbon,2,0)

Surface\_Ct(t) = Surface\_Ct(t-dt) + (Air\_Sea\_Exchange +  
Upwelled\_Carbon-Downwelled\_Carbon-PartC-CaCO3) \*

dt

INIT Surface\_Ct = 219

INFLOWS:

Air\_Sea\_Exchange =

Piston\_Velocity\*((Atmospheric\_CO2/1e6)-  
((Surface\_Ct/1e5)\*Alpha0))

Upwelled\_Carbon = (Bottom\_Ct/3400)\*Upwelling\_Rate

OUTFLOWS:

Downwelled\_Carbon = (Surface\_Ct/100)\*Upwelling\_Rate

PartC = (Part\_NO3\*C:NO3\_Ratio)

CaCO3 = 15

Atmospheric\_PCO2 = (Atmospheric\_CO2/1e6/3.16e-2)\*1e6

Piston\_Velocity = 3e3

Upwelling\_Rate = 130

Fe Module

Bottom\_Fe(t) = Bottom\_Fe(t-dt) + (Downwelled\_Fe +  
Part\_Fe +

Fe\_Remineralization + Fe\_CaCO3-Upwelled\_Fe-  
Sediment\_Rate\_of\_Iron-Advection) \* dt

INIT Bottom\_Fe = 4.08e-8

INFLOWS:

Downwelled\_Fe = (Surface\_Fe/100)\*Upwelling\_Rate

Part\_Fe = Part\_NO3\*Fe:NO3\_Ratio

Fe\_Remineralization = delay(Sediment\_Rate\_of\_Iron,2,0)

Fe\_CaCO3 = N\_CaCO3\*Fe:NO3\_Ratio

OUTFLOWS:

Upwelled\_Fe = (Bottom\_Fe/3400)\*Upwelling\_Rate

Sediment\_Rate\_of\_Iron = (Part\_NO3\*Fe:NO3\_Ratio)\*.01

Advection = Aeolian\_Fe\_Flux

Sedimentary\_Fe(t) = Sedimentary\_Fe(t-dt) +  
(Sediment\_Rate\_of\_Iron-Fe\_Remineralization) \* dt

INIT Sedimentary\_Fe = 0

INFLOWS:

Sediment\_Rate\_of\_Iron = (Part\_NO3\*Fe:NO3\_Ratio)\*.01

# OUTFLOWS:

```

Fe_Reminerlization = delay(Sediment_Rate_of_Iron,2,0)
Surface_Fe(t) = Surface_Fe(t-dt) + (Upwelled_Fe +
Aeolian_Fe_Flux-Downwelled_Fe-Part_Fe-Fe_CaCO3) * dt
INIT Surface_Fe = 2.6e-8

```

# INFLOWS:

```

Upwelled_Fe = (Bottom_Fe/3400)*Upwelling_Rate
Aeolian_Fe_Flux = 16*2.048835e-7

```

# OUTFLOWS:

```

Downwelled_Fe = (Surface_Fe/100)*Upwelling_Rate
Part_Fe = Part_NO3*Fe:NO3_Ratio
Fe_CaCO3 = N_CaCO3*Fe:NO3_Ratio
Conc_of_Surface_Fe = Surface_Fe/100000
Fe:NO3_Ratio = 1.65e-4
Fe_ConB = Bottom_Fe/3400000
Nitrate Module
Bottom_NO3(t) = Bottom_NO3(t-dt) + (Part_NO3 +
      Downwelled_NO3 + NO3_Reminerlization + N_CaCO3-
      Sediment_Rate_of_NO3-Upwelled_NO3) * dt
INIT Bottom_NO3 = 102

```

# INFLOWS:

```

Part_NO3 =
(Vmax_N*Conc_of_Surface_Fe/(Ks_FE+Conc_of_Surface_Fe))
Downwelled_NO3 = (Surface_NO3/100)*Upwelling_Rate
NO3_Reminerlization = delay(Sediment_Rate_of_NO3,2,0)
N_CaCO3 = CaCO3/C:NO3_Ratio

```

# OUTFLOWS:

```

Sediment_Rate_of_NO3 = Part_NO3*.01
Upwelled_NO3 = (Bottom_NO3/3400)*Upwelling_Rate
Sedimentary_NO3(t) = Sedimentary_NO3(t-dt) +
      (Sediment_Rate_of_NO3-NO3_Reminerlization) * dt
INIT Sedimentary_NO3 = 0.07

```

# INFLOWS:

```

Sediment_Rate_of_NO3 = Part_NO3*.01

```

# OUTFLOWS:

```

NO3_Reminerlization = delay(Sediment_Rate_of_NO3,2,0)
Surface_NO3(t) = Surface_NO3(t-dt) + (Upwelled_NO3-
Part_NO3-
      Downwelled_NO3-N_CaCO3) * dt

```

INIT Surface\_NO3 = 1.2000

INFLOWS:

Upwelled\_NO3 = (Bottom\_NO3/3400)\*Upwelling\_Rate

OUTFLOWS:

Part\_NO3 =

$(V_{\max\_N} \cdot \text{Conc\_of\_Surface\_Fe} / (K_{s\_FE} + \text{Conc\_of\_Surface\_Fe}))$

Downwelled\_NO3 = (Surface\_NO3/100)\*Upwelling\_Rate

N\_CaCO3 = CaCO3/C:NO3\_Ratio

C:NO3\_Ratio = 6.6

Conc\_of\_Surf\_NO3 = Surface\_NO3/100000

Ks\_FE = 5e-12

NO3\_ConB = Bottom\_NO3/3400000

Vmax\_N = .55