A biogeochemical model of phytoplankton productivity in an urban estuary: The importance of ammonium and freshwater flow

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A R T I C L E   I N F O

Article history:
Received 3 February 2013
Received in revised form 14 May 2013
Accepted 15 May 2013
Available online 20 June 2013

Keywords:
Phytoplankton
Ammonium
Nitrate
Estuary
Bloom
Freshwater flow
Suisun Bay
Regional Index Terms: USA
California
San Francisco Bay

A B S T R A C T

Increased discharge of ammonium (NH₄) to the San Francisco Estuary (SFE), largely in treated domestic sewage effluent, has been linked to chronically food-limited conditions and to reduced fish abundance. Elevated chlorophyll concentrations at phytoplankton bloom levels are rarely observed if the ambient NH₄ concentrations are above 4 μmol L⁻¹—the NH₄ paradox. In both field samples and water held in enclosures for one week, an inverse relation was observed between NH₄ concentrations and nitrate (NO₃) uptake by phytoplankton, likely a result of inhibition of NO₃ uptake by NH₄. A simple model was constructed to examine the interaction between NH₄ and NO₃ inputs to the estuary, with varying freshwater river flow (hereafter termed flow) conditions. Sensitivity analyses were made and initial model parameters taken from an existing oceanic biogeochemistry model. Experiments were made with the model, and showed that initial NH₄ concentrations largely controlled the length of time to peak NO₃ uptake and NO₃ exhaustion. The model parameters were then tuned using observations from a set of enclosure experiments, and validated with results from a series of independent enclosure experiments with a variety of initial conditions. The model was run in three flow modes: (1) with no (zero) flow, (2) with flow, a fully mixed water column and a uniform light field, and (3) with flow, a fully mixed water column but with light attenuation and depth integrated values of N uptake. In the zero flow mode the model simulated enclosure experiments and when compared with enclosure results indicated the basic NH₄–NO₃ interactions to be correctly represented in the model. In the modes with flow, the model simulations reproduced a sharp transition from high phytoplankton productivity using both NO₃ and NH₄ to low productivity using only NH₄, simulating the historical effects of increasing NH₄ inputs to the SFE. With vertical integration to incorporate effects of irradiance, sharp boundaries at specific combinations of varying flow and NH₄ inputs were observed. The model could be embedded into three dimensional models of the SFE/Delta currently being implemented for management purposes such as regulating estuarine nutrients as required by the State of California and evaluating the effects of water management decisions on salmon and protected species of fish.

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1. Introduction

In the urban San Francisco Estuary (SFE) a rapid decline of four fish species to low population levels suggests that some may be on the verge of extinction. The trend is known as the Pelagic Organism Decline (POD) and a search for the cause(s) has been in progress (e.g. Sommer et al., 2007). Studies have concluded that most levels of the food web above the primary producers are food limited (Müller-Solger et al., 2002; Kimmerer et al., 2005; Sobczak et al., 2005; Greene et al., 2011). The estuary has chronically low primary production (Kimmerer et al., 2012) near the bottom of estuaries listed in order of annual primary production (Boynton et al., 1982; Nixon, 1988). Suisun Bay in the northern SFE (Fig. 1) is a center of attention about the causes of the POD since it is where critical phases in the life cycle of one POD species occur. This species, the delta smelt (Hypomesus transpacificus), has been listed as endangered under the California Endangered Species Act since 2008.

Although the current debate on the cause(s) of the POD focuses on the period from 2000 to the present, the primary productivity of the SFE has been declining for more than three decades (Jassby et al., 2002) even though water transparency, previously shown to determine primary production in the SFE (Coles and Cloern, 1984), and nutrient loads have been increasing over the same period (Jassby, 2008). This situation with declining productivity and high nutrients has been termed oligotrophication by Nixon (1990). A trend of increasing chlorophyll in the Delta has occurred in the period 1996–2005, but not in Suisun Bay (Jassby, 2008).

Before 1980, Suisun Bay was characterized as a high chlorophyll ecosystem dominated by diatoms and large zooplankton (Ball and Arthur, 1979); it is now dominated by small phytoplankton,
small zooplankton (Gilbert et al., 2011) and low primary production (Kimmerer et al., 2012). High summer chlorophyll concentrations in Suisun Bay declined to low levels in 1987. Additionally spring blooms were not observed in Suisun Bay (Dugdale et al., 2012). The invasive Asian overbite clam (Potamocorbula amurensis) appeared in substantial numbers at that time and is considered the primary reason for the crash in phytoplankton biomass (Alpine and Cloern, 1992). However clam populations are low in spring (Greene et al., 2011) and grazing is insufficient to explain the lack of spring blooms. Nutrients had been neglected as a factor in regulation of primary production in the SFE as N, Si and P were all in excess of requirements throughout the year (Jassby et al., 2002). However, the decline in chlorophyll in Suisun Bay (in all seasons) began at about the same time as NH₄ discharge and concentrations began to increase rapidly in the Sacramento River the main water source for Suisun Bay (Gilbert et al., 2011), the result of both increases in urban populations and agricultural use of nitrogen fertilizers (Jassby, 2008). In 1984 there were 5.2 tons NH₄-N day⁻¹ added to the Sacramento River at Freeport from municipal waste (Schemel and Hager, 1986); additional natural/agricultural NH₄ in the Sacramento River was less than or equal to half of the effluent input. Today, discharge of NH₄ at Freeport is about 15 tons NH₄-N per day (Jassby, 2008).

A growing body of evidence points to NH₄ inputs of anthropogenic origin as a driving factor in the decline and eventual collapse of the primary productivity of the northern SFE and in particular of Suisun Bay (e.g. Dugdale et al., 2007; Gilbert et al., 2011; Dugdale et al., 2012). Measurements of dissolved inorganic N(DIN) uptake by phytoplankton using incubations with ¹⁵NO₃ and ¹⁵NH₄ as tracers have indicated that nutrients in SFE are important in determining phytoplankton productivity (Wilkerson et al., 2006; Dugdale et al., 2007, 2012; Parker et al., 2012a,b). NO₃ is rarely used in the SFE/Delta as a consequence of suppression of NO₃ uptake by NH₄ with phytoplankton blooms occurring in the SFE only when NH₄ concentrations declined to low levels (Wilkerson et al., 2006; Dugdale et al., 2007). NO₃ uptake is essential for high productivity rates and phytoplankton bloom occurrence as NO₃ is the largest reservoir of DIN in the SFE (Wilkerson et al., 2006; Dugdale et al., 2012). Decreased phytoplankton growth rates and reduced carbon fixation (primary production) occurred when the algae were using NH₄ compared to NO₃ (Wilkerson et al., 2006; Parker et al., 2012a).

When chlorophyll concentrations and NO₃ uptake rates were plotted against NH₄ concentration, a threshold of about 4 μmol L⁻¹ NH₄ appeared to delineate the level at which suppression of NO₃ uptake occurred. Below this concentration, NO₃ uptake was enabled and occurred even more rapidly when NH₄ concentrations decreased to ~1 μmol L⁻¹ accompanied by a rapid increase in chlorophyll (Dugdale et al., 2007).

To understand the sequence of events involved in the NH₄ response by phytoplankton, to use in simulation models, experiments were made with water from Central San Francisco Bay that was enclosed and incubated under natural light. The phytoplankton response in the enclosed water followed the pattern shown in Fig. 2 (taken from Dugdale et al., 2007) that has been repeatedly observed (e.g. Parker et al., 2012a). First NH₄ concentrations decreased and then NO₃ concentrations decreased rapidly to zero within four days (Fig. 2a and b) (Dugdale et al., 2007). During this four day cycle, the biomass-specific NO₃ uptake rate (VNO₃) increased to a peak at Day 2 or 3 and then declined rapidly as NO₃ was depleted (Fig. 2c). The biomass-specific NH₄ uptake rate (VNH₄) remained relatively unchanged or decreased (Fig. 2d). Chlorophyll accumulation (Fig. 2e) occurred as NO₃ was drawn down. This rapid use of NO₃ observed in SFE water is virtually identical to that observed in newly upwelled ocean water (Wilkerson and Dugdale, 1987; Dugdale et al., 2006) and incorporated into a productivity model that included acceleration or “shift up” of NO₃ uptake rates (Dugdale et al., 1990). The essential feature of this shift-up model is that the biomass specific NO₃ uptake rate, VNO₃ (equivalent to a nitrogen-based growth rate) increases at a rate proportional to the ambient NO₃ concentration. Since NO₃ is usually
Fig. 2. Time course in enclosures filled with Central Bay water of (a) NO$_3$ and NH$_4$ concentrations in enclosures with low initial NH$_4$ (Enclosures A and B); (b) NO$_3$ and NH$_4$ concentrations in enclosures with high initial NH$_4$ (Enclosures C, D, E, F); (c) specific uptake rates of NO$_3$; (d) specific uptake rates of NH$_4$; (e) chlorophyll concentration (from Dugdale et al., 2007).
the largest DIN pool in the SFE this will lead to enhanced growth when it is used compared to NH$_4$, that is typically the smaller pool of DIN. The effect can be seen in the VNO$_3$ vs. elapsed time curve for enclosure D (Fig. 2c) which has the steepest slope and is the enclosure with the highest initial NO$_3$ concentration (Fig. 2b). Consequently, VNO$_3$ increases with time until NO$_3$ concentration falls to the Michaelis-Menten limiting range for uptake. This accounts for the result, that all NO$_3$ is exhausted by the phytoplankton in the same length of time, about 4 days, regardless of the initial ambient NO$_3$ (Fig. 2a and b).

In the northern SFE rare spring blooms are enabled by access to the NO$_3$ pool accompanied by high productivity rates when NH$_4$ concentrations are low (Wilkerson et al., 2006; Dugdale et al., 2012). In the period 2000–2010, in Suisun Bay, only two phytoplankton blooms were observed in Suisun Bay: the first in 2000 (Wilkerson et al., 2006) and a second in 2010 (Dugdale et al., 2012). Both blooms (>30 μg L$^{-1}$ chlorophyll) occurred when NH$_4$ concentrations were about 1 μmol L$^{-1}$ (Dugdale et al., 2012). Dugdale et al. (2012) developed a conceptual model for the prediction of blooms in Suisun Bay with three required criteria (NH$_4$ loading criterion, NH$_4$ concentration criterion and a washout river flow criterion). This analysis highlighted the combined importance of freshwater (river) flow and NH$_4$ concentration in determining bloom initiation in the northern SFE.

A more complete understanding of the role of anthropogenic NH$_4$ and flow in modulating productivity in the SFE will require the development of linked biogeochemical and hydrodynamic models. Here, we evaluate potential productivity of Suisun Bay using a simple biogeochemical model. The model is based on results from field and enclosure experiments conducted in the northern SFE and constructed to be run in a three modes: (1) with no (zero) flow, (2) with flow, a fully mixed water column and a uniform light field, and (3) with flow, a fully mixed water column but with light attenuation and depth integrated values of N uptake. From resulting model runs we make predictions for the potential effects of managed perturbations in the Suisun Bay ecosystem, e.g. reduction in allowable discharge of anthropogenic NH$_4$ in sewage effluent and/or changes in freshwater flow.

2. Model development and construction

Our strategy was to construct a biogeochemical simulation model, linking NH$_4$ and NO$_3$ inputs, phytoplankton uptake, and freshwater flow, make initial runs with zero flow (mode 1) to compare with data collected using enclosure experiments, and then tune the model as necessary to reproduce the observed effect of NH$_4$ on NO$_3$ uptake. The model was tested (without flow) against an independent data set from enclosure experiments. Finally the model was run with added freshwater flow effects (modes 2 and 3). The model was constructed and run using Stella 10.0 (Ieesystems.com). The flows and controls are shown in Fig. 3 and the parameters listed in Table 1 with the values used for different model runs in Table 2. The currency of the model is nitrogen and the pools are NO$_3$, NH$_4$, and particulate nitrogen (PON). Inflows and outflows are allowed for all three pools. In constructing this model, we drew upon our previous work in developing a biogeochemical ecosystem model — the CoSiNE (Carbon, Silicate, Nitrogen Ecosystem) model (Chai et al., 2002; Dugdale et al., 2002) that has been incorporated into Pacific basin-wide and coastal ROMS models (e.g. Xi and Chai, 2012), reproducing many important features of these ecosystems. The present model incorporates CoSiNE phytoplankton uptake kinetics (Michaelis-Menten formulation) and an exponential function ($\psi$) for NH$_4$ inhibition of NO$_3$ uptake (Chai et al., 2002).

The SFE biogeochemical model incorporates kinetic parameters from the CoSiNE model (Chai et al., 2002), appropriate for diatoms which are the major functional group that dominates the final population in enclosure experiments in SFE and in phytoplankton blooms in Suisun Bay (Parker et al., 2012a; Dugdale et al., 2012; Cloern and Dufford, 2005). Diatoms are fast-growing and outcompete other phytoplankton in high nutrient conditions, e.g. in coastal upwelling. They prefer, and under some conditions physiologically require NO$_3$ over NH$_4$ (Syrett, 1981; Berg et al., 2001; Gilbert et al., 2006). The model incorporates the concept of shift up, i.e. acceleration of NO$_3$ uptake which is not included in the CoSiNE formulation. The formulation for the acceleration of NO$_3$ uptake ($A$) to calculate maximum specific NO$_3$ uptake is a function of NO$_3$ concentration as used in Dugdale et al. (1990). The model is run with a time step of

![Fig. 3. Diagram of the biogeochemical model showing flows of NH$_4$, NO$_3$ and PON (thick arrows) and control processes in dotted lines including acceleration of VNO$_3$ by NO$_3$ and inhibition of VNO$_3$ by NH$_4$.](image-url)
Table 2

Values used for model parameters in different runs; parameters kept constant in all runs were initial VNO3 = 0.03 h⁻¹, β = 4 × 10⁻⁵, ψ = −5.39, KsNH₄ = 1 μmol L⁻¹, KsNO₃ = 1 μmol L⁻¹.

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<th>NO₃(i)(μmol L⁻¹)</th>
<th>PON(i)(μmol L⁻¹)</th>
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one hour, consistent with the units reported for the kinetic parameters for N uptake. The model is stable at this time step and no gain in precision is likely to be achieved by using smaller time steps. To evaluate daily rates, since NO₃ uptake occurs over 12 h and NH₄ uptake over 18 h (Wilkerson et al., 2000) each hourly rate is multiplied by 0.5 for NO₃ uptake and by 0.75 for NH₄.

Equations governing the model are:

To determine NH₄ balance in an embayment:

\[ \text{NH}_4(t) = \text{NH}_4(t - dt) + (\text{NH}_4\text{ inflow} - \rho\text{NH}_4 - \text{NH}_4\text{ outflow}) \times dt \]  

(1)

where NH₄(t) is NH₄ after time t; dt is the time interval (1 h) and

\[ \text{NH}_4\text{ inflow} = \text{NH}_4(i) \times \text{flow} \]  

(2)

\[ \rho\text{NH}_4 = V\text{NH}_4 \times \text{PON} \times 0.75 \]  

(3)

where VNH₄ is biomass specific uptake rate (h⁻¹) and PON is particulate organic nitrogen concentration (i.e. phytoplankton biomass) and NH₄(i) is initial NH₄ concentration.

\[ \text{NH}_4\text{ outflow} = \text{NH}_4 \times \text{flow} \]  

(4)

To determine NO₃ balance:

\[ \text{NO}_3(t) = \text{NO}_3(t - dt) + (\text{NO}_3\text{ inflow} - \rho\text{NO}_3 - \text{NO}_3\text{ outflow}) \times dt \]  

(5)

\[ \text{NO}_3\text{ inflow} = \text{NO}_3(i) \times \text{flow} \]  

(6)

\[ \rho\text{NO}_3 = V\text{NO}_3 \times \text{PON} \times 0.5 \]  

(7)

\[ \text{NO}_3\text{ outflow} = \text{NO}_3 \times \text{flow} \]  

(8)

To determine PON balance:

\[ \text{PON}(t) = \text{PON}(t - dt) + (\rho\text{NO}_3 + \rho\text{NH}_4 + \text{PON inflow} - \text{PON outflow}) \times dt \]  

(9)

PON inflow = PON(i) × flow  

(10)

PON outflow = PON × flow  

(11)

To determine phytoplankton uptake rates

\[ V\text{NH}_4 = V_{\text{max}}\text{NH}_4 \times \frac{\text{NH}_4}{\text{NH}_4 + K_s\text{NH}_4} \]  

(12)

\[ V\text{NO}_3 = (V\text{NO}_3(i) + A \times t) \times \frac{\text{NO}_3}{K_s\text{NO}_3 + \text{NO}_3} \times \exp(-\gamma \times \text{NH}_4) \]  

(13)

\[ A = \alpha \times \text{NO}_3 + \beta \]  

(14)

where \( A \) is acceleration of uptake, \( K_s\text{NH}_4 \) and \( K_s\text{NO}_3 \) are half saturation constants, \( \Psi \) is a constant for NH₄ inhibition of NO₃ uptake.

The equations unique to this model are the inhibition of NO₃ uptake by NH₄, by an exponential effect with parameter \( \Psi \) and the increase of maximal NO₃ uptake with time by the acceleration term \( A \). The term \( A \) has two elements, \( \alpha \) which is multiplied by the ambient NO₃ concentration, and a constant \( \beta \) (Dugdale et al., 1990); both have units of t⁻². \( \alpha \) is the more important element. For example, with NO₃ = 30 μmol L⁻¹, elapsed time of 240 h, and \( \alpha = 4 \times 10^{-5} \) h⁻², an increase of VNO₃ of 0.29 h⁻¹ results while \( \beta \) × t for the same period results in an increase of only 0.01 h⁻¹, about 3% of the increase due to \( \alpha \). Parameters used in each model run and associated with each figure are provided in Table 2. For the initial model runs to simulate enclosures, the values of \( \Psi \) were taken from Chai et al. (2002). Data supplied to the model are initial concentrations of NH₄, NO₃ and PON and in modes 2 and 3, freshwater flow.

3. Model runs with zero flow

3.1. Model run with zero flow, variable initial NO₃, high initial NH₄ concentration

The way the model works is illustrated in Fig. 4, the results of model runs at two initial NO₃ concentrations (20 or 30 μmol L⁻¹) and initial NH₄ at 6 μmol L⁻¹. No change in NO₃ concentration
occurs until NH₄ concentration declines to low, non-inhibiting concentrations as a result of NH₄ uptake by the phytoplankton (Fig. 4a). The time to exhaust the initial NO₃ is the same for both conditions, 96 h, regardless of the initial NO₃ concentration, as previously described for the shift-up model (Dugdale et al., 1990). The processes leading to this result occur in a sequence. First, there is an increase in NO₃ uptake on a biomass basis (VNO₃) associated with increasing NO₃ concentration, which peaks at 72 h (Fig. 4b). This increase in uptake is a result of the acceleration term, A (Eqs. (13) and (14)) such that the initial slope of the VNO₃ vs. time curve is steeper for the higher NO₃ concentration. The peak VNO₃ (Fig. 4b) occurs as NO₃ concentrations decline (Fig. 4a), acceleration rates decrease and VNO₃ begins to decline (Fig. 4b). The peak VNO₃ is higher for the higher initial NO₃ concentration as a result of the higher initial acceleration rates. The timing of the VNO₃ peak, at about 72 h for both initial NO₃ concentrations is largely dependent on the shape of the NO₃ concentration versus time curve (Fig. 4a). For the first 60 h, biomass (PON) increases at a relatively low rate due to NH₄ uptake and then increases rapidly (Fig. 4d) as NO₃ uptake begins. The actual (transport) uptake rate ρNO₃ is the product of VNO₃ and PON concentration, (Eq. (7)). In the low NH₄ period VNO₃ is increasing and PON is also accumulating with the result that a rapid increase in ρNO₃ occurs (Fig. 4c). The peak in ρNO₃ (Fig. 4c; 79 h) occurs slightly later than the peak VNO₃ (Fig. 4b; 72 h) delayed due to the continuing accumulation of biomass as PON partially compensating for the decline in VNO₃. The final result is a more rapid increase in PON and a higher concentration of PON with the higher initial NO₃.

3.2. Model run with zero flow, variable initial NO₃, low initial NH₄ concentration

With lower initial NH₄ concentration (i.e. 2 μmol L⁻¹), and initial NO₃ of 20 or 30 μmol L⁻¹, NO₃ concentration (Fig. 5a) declines earlier than in the high NH₄ concentration runs (Fig. 4a). The time of NO₃ exhaustion (at 96 h) is virtually the same for the different initial NO₃ values, (Fig. 5a) and at high NH₄ initial concentrations (Fig. 4a). The peak values of VNO₃ are still a direct function of the initial NO₃ concentration (Fig. 5b), but the curves are broader with time and occur about 10 h earlier (at 62 h elapsed time) than with higher initial NH₄ concentration (Section 3.1, Fig. 4b). The NO₃ uptake (ρNO₃) curves (Fig. 5c) are broader in the low NH₄ runs. As in the high initial NH₄ runs, the uptake peaks of ρNO₃ (Fig. 5c) are delayed relative to VNO₃ (Fig. 5b), a result of the delay in accumulation of biomass as PON (Fig. 5d). As in the runs with high NH₄ concentration, these patterns are controlled largely by the rates of decline of NO₃, which starts earlier in the low NH₄ runs, but ends at the same time as the high NH₄ concentration runs, a consequence of the shift-up model.
property of NO₃ exhaustion occurring at a relatively constant time regardless of the initial NO₃ concentration.

3.3. Sensitivity analysis

3.3.1. Effects of parameters on the time to NO₃ depletion to zero

The NH₄ uptake rate determines the elapsed time before NO₃ uptake occurs. The value of KₛNH₄ affects the rate of NH₄ uptake (Eq. (12)) and a sensitivity analysis was made of the influence of KₛNH₄ on the model output. The time to zero NO₃ appears as a linear function of KₛNH₄ (Fig. 6a) but the dependence of the time to NO₃ exhaustion was not very sensitive to the value of KₛNH₄, increasing the time to exhaustion by only 40 h, from 120 to 160 h. Diatoms are components of the ecosystem that are of the “r” type that compete on the basis of fast growth rates rather than on the ability to take up nutrients at low concentrations i.e. low Kₛ. High growth rates (Vₘₐₓ) are usually correlated with high Kₛ values. The effect of different initial NH₄ concentrations on the time to exhaustion was shown to be small in model runs (Figs. 4 and 5) so it would be expected that KₛNH₄ values also have little effect on time to exhaustion.

The effect of KₛNO₃ is small as it occurs only late, when NO₃ concentration drops rapidly (not shown). The time to NO₃ exhaustion is strongly dependent on the acceleration term, in particular the element α. With α = 0 h⁻¹, the time to NO₃ exhaustion is about 220 h, but drops to 110 h at α = 4 × 10⁻⁵ h⁻² with little changes at higher values (Fig. 6b). The value of ψ has little effect on the time for NO₃ exhaustion (Fig. 6c).

3.3.2. Effects of parameters on peak VNO₃ and time of peak VNO₃

The value of KₛNH₄ has little effect on the peak value of VNO₃ (Fig. 6d), but affects the time that peak VNO₃ is reached (Fig. 6d), from −50 h at KₛNH₄ = 0 μmol L⁻¹ to nearly 150 h at KₛNH₄ = 3 μmol L⁻¹, a 3-fold increase. The peak value of VNO₃ is a nearly linear function of α, increasing from 0.02 to 0.12 h⁻¹ at α = 10 × 10⁻⁵ h⁻² (Fig. 6e). The time at which the peak value of VNO₃ is reached occurs at 180 h with α = 0 h⁻² and drops to 60 h at α = 1 × 10⁻⁵ h⁻²; little change in VNO₃ occurs at higher α (Fig. 6e). The greatest effect of ψ on VNO₃ and time to peak VNO₃ is observed between ψ = 0 (no inhibition) to ψ = −2; above that value little change in VNO₃ occurs (Fig. 6f).

Responses to ±50% changes in parameters from the standard model run conditions are shown in Table 3. Changes in KₛNH₄ result in little change in time to NO₃ exhaustion or to peak VNO₃, but a −50% change in KₛNH₄ results in a −15% change in time of the peak VNO₃. The 50% perturbation of α results in a +20% and −10% change in time to NO₃ exhaustion, a −38% to +35% change in peak VNO₃, and a +10% to −3% change in time of peak VNO₃. The maximum response due to a 50% perturbation of ψ is a 4% reduction in peak VNO₃.

3.4. Model calibration, zero flow mode (to simulate enclosures)

Trials of the model were first made using initial input parameters from a series of enclosure experiments (Enclosure A (experiment named 9901), Enclosure C (9903) and Enclosure E...
(9905A), described Dugdale et al. (2007) (Fig. 2). Water collected in Central Bay (Fig. 1), was incubated under natural light attenuated by 50% with window screening and cooled with running bay water. NO$_3$ and NH$_4$ uptake rates were obtained using $^{15}$N tracers. Enrichments were at 10% $^{15}$N to avoid increases in concentration-forced uptake rates (Dugdale and Wilkerson, 1986). Modeled NH$_4$ and NO$_3$ concentration (obtained using the initial NH$_4$, NO$_3$, PON) in enclosures and observed enclosure data are plotted against time in Fig. 7a, d, g for three enclosures. In all cases a good visual fit of the modeled NH$_4$ and observed data is obtained. Modeled concentrations of NO$_3$ using $\alpha = 4 \times 10^{-5}$ h$^{-2}$ to calculate acceleration of uptake A, do not decline rapidly enough to fit the data. However, when the model is run with $\alpha = 8 \times 10^{-5}$ h$^{-2}$, a good visual fit is obtained. Plots of NO$_3$ vs. time for two additional values of $\psi$, $-1.0$ and $-2.0$ with $\alpha = 8 \times 10^{-5}$ h$^{-2}$ (Fig. 7a) show very little change, consistent with results in Table 3, Section 3.3. The small number of experimental data points makes it difficult to make standard statistical evaluations. However, the mean difference for NH$_4$ concentration between model and observations for all three enclosures was 0.3 $\mu$mol L$^{-1}$ with a standard deviation of 0.4 $\mu$mol L$^{-1}$. For NO$_3$, the mean difference between model and observed data was −0.7 $\mu$mol L$^{-1}$ with a standard deviation of 2.3 $\mu$mol L$^{-1}$.

Modeled $\rho$NO$_3$ are plotted along with enclosure data (Fig. 7b, e, h) for simulations run at $\alpha = 8 \times 10^{-5}$ h$^{-2}$. The visual fit is good except for the Day 4 point for enclosure A (9901) (Fig. 7b) when measured NO$_3$ concentration was zero but a positive uptake rate was measured, an artifact of added tracer $^{15}$NO$_3$. The mean difference between model and observed data for $\rho$NO$_3$ was 0.1 $\mu$mol L$^{-1}$ h$^{-1}$ with a standard deviation of 0.12 $\mu$mol L$^{-1}$ h$^{-1}$. The simulated pattern of VNO$_3$ (Fig. 7c, f, i) has the same pattern as $\rho$NO$_3$ but VNO$_3$ (Fig. 7c, f, i) are well simulated, with more

![Fig. 6. Sensitivity analyses: the effect of (a) $K_{\text{NH}_4}$; (b) $\alpha$; (c) $\psi$. on the elapsed time taken for NO$_3$ to reach zero, and of (d) $K_{\text{NH}_4}$; (e) $\alpha$; (f) $\psi$ on the peak value of VNO$_3$ and the elapsed time to reach peak VNO$_3$.](image-url)

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<th>%change from standard run</th>
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Fig. 7. Time course of modeled (lines) enclosure nutrient concentration (a, d, g), $\rho$NO$_3$ uptake data (b, e, h) and VNO$_3$ (c, f, i) compared with observed enclosure data (symbols, □ for NO$_3$, ○ for NH$_4$) for three sets of enclosure experiments made using water from Central Bay (a-c, Enclosure A, d-f Enclosure C, g-i, Enclosure E) that had different initial conditions. (a) concentrations of NO$_3$ and NH$_4$ with $\alpha = 4 \times 10^{-5} \text{ h}^{-2}, \psi = -5.59$ (solid line); $\alpha = 8 \times 10^{-5} \text{ h}^{-2}, \psi = -5.59$ (dashed line); $\alpha = 8 \times 10^{-6} \text{ h}^{-2}, \psi = -2$ (dotted line); (d, g) concentrations of NO$_3$ and NH$_4$ with $\alpha = 4 \times 10^{-5} \text{ h}^{-2}, \psi = -5.59$ (solid line); $\alpha = 8 \times 10^{-5} \text{ h}^{-2}, \psi = -5.59$ (dashed line).

variability in the observed data due to the presence of detrital-N in the PON pool being measured using mass spectrometry. However, the values of $\rho$NO$_3$ are robust as any detrital particulate N that dilutes the VNO$_3$ is canceled by the higher PON (Dugdale and Wilkerson, 1986). The only parameter that was varied to obtain a fit of the model and Central Bay enclosure data concentration pattern with time was $\alpha$ in the calculation of acceleration, A.

3.5. Model validation using independent data

Initial data were used from independent observation data sets of enclosures filled with water from Central and Suisun Bays and Sacramento and San Joaquin rivers to initialize the model and compare modeled uptake rates and biomass accumulation with observed data.

3.5.1. Enclosures from the Central Bay ("XB2003") experiment

Manipulated enclosure experiments (XB2003) were made in which additions of NH$_4$ were made, at 5, 10, 20 and 30 $\mu$mol L$^{-1}$ to water collected from Central Bay (Fig. 1) and the effects followed for four days (see Dugdale et al., 2007). Each enclosure was sampled daily for nutrient and chlorophyll concentrations, and $^{15}$NH$_4$ and $^{15}$NO$_3$ uptake incubations made with 50% ambient irradiance, cooled with flowing bay water.

The time course of modeled concentrations of NO$_3$ and NH$_4$, and uptake are plotted along with the data from the five enclosures in Fig. 8a–j. The modeled exhaustion point for NH$_4$ (i.e. to reach zero)
is well simulated for all enclosures (Fig. 8a–e) with some indications of initial lag in the measured decline in NH4 in the two highest NH4 addition enclosures, 20 and 30 μmol L−1 (Fig. 8d and e). The initiation of NO3 drawdown is progressively delayed by increasing NH4 additions (Fig. 8a–e), and is correlated with the decrease in NH4 to low or near zero concentrations. At 30 μmol L−1 NH4 (Fig. 8e), NO3 drawdown is not observed even by the final day of the experiment. ρNO3 (Fig. 8f–j) is progressively delayed with increasing NH4 concentration. However, the peak ρNO3 increases with increasing NH4 concentration up to 20 μmol L−1, a result of the increased time for acceleration of the NO3 uptake rate. This increase in peak ρNO3 at later times in the incubation allows all NO3 to be assimilated by Day 4, the exception is at the 30 μmol L−1 where little NO3 uptake occurs even at that time.

3.5.2. Enclosures from the Sacramento River (“WB09-1′”) experiment
Enclosure experiments (WB09-1 series) were made with water collected from the Sacramento River, at Garcia Bend, above the Sacramento Regional Waste Water Treatment Plant and at location RM44, below the Plant outfall. Three Garcia Bend experiments were conducted, one with no N amendments, a second with added NH4 and a third with added NO3. The RM44 enclosure was not amended. All enclosures were followed for 10 days. Daily samplings were made for nutrients and chlorophyll and for 15N tracer uptake rate measurements at 50% ambient light.

The time series of modeled N concentration and uptake (with α = 8 × 10−5 h−2) and measured data are show in Fig. 9a–h. The un-amended Garcia Bend enclosure time series of NO3 and NH4 drawdown (Fig. 9a) is very similar to the low NH4, high NO3 enclosure using Central Bay water (Fig. 7a). With added NH4 to Garcia Bend water (Fig. 9c) modeled NO3 and NH4 drawdown are delayed similar to the pattern in the manipulated Central Bay enclosure with 5 μmol L−1 NH4 added (Fig. 8b), and also very similar to the RM44 enclosure (Fig. 9g) which had elevated initial NH4 and NO3. The modeled NO3 in the NO3 amended Garcia Bend enclosure (Fig. 9e) was exhausted one day earlier than was observed in the enclosure.
In the two high NH₄ enclosures, ρNH₄ as modeled overestimated the measured uptake rates (Fig. 9d and h), but the agreement between time series of modeled and observed NH₄ concentrations (Fig. 9c and g) suggests the measured ¹⁵N uptake data may be in error. Modeled ρNO₃ was in good agreement with measured rates in the un-amended Garcia Bend and RM44 enclosures (Fig. 9b and h), but were higher than measured uptake in the two amended enclosures (Fig. 9d and f) suggesting a problem with the ¹⁵N measurements. In the case of the NO₃ amended Garcia Bend enclosure (Fig. 9e and f) the modeled increase in ρNO₃ due to shift-up (acceleration) by increased NO₃ did not occur in the measured enclosure results. The measured peak in ρNO₃ in the enclosure would have occurred after 4 days, as NO₃ was drawn down in the enclosure (Fig. 9e). However, no uptake measurements with ¹⁵NO₃ were made at that time.

3.5.3. Enclosures from the northern Estuary (“Bad Suisun 3”) experiment

A set of enclosures with water collected in Central Bay, Suisun Bay, Rio Vista in the Sacramento River and at Ward Island in the lower San Joaquin River (Fig. 1) were sampled daily as in the previous experiments. Concentrations and uptake of NH₄ and NO₃ are plotted against elapsed time in Fig. 10a–h. Modeled drawdown of NH₄ and measured data (Fig. 10a, c, e, g) are in very good
agreement with Central Bay and Suisun Bay (Fig. 10a and c) but not for Rio Vista and San Joaquin (Fig. 10e and g) where no change in NH₄ occurred until Day 4 in the enclosures. The timing of modeled NO₃ decline in the Central Bay enclosure was slower than the measured data, but measured pattern is correct (Fig. 10a). The modeled peak and timing of pNO₃ in Central Bay (Fig. 10b) are in agreement during the first two days, but measured pNO₃ in Days 3 and 4 when the NO₃ concentrations were zero was likely an artifact of the added NO₃ substrate as part of the ¹⁵N inoculation.

Modeled NH₄ decline and observed data are in agreement in the Suisun Bay enclosure (Fig. 10c). However, measured NO₃ declined more slowly than modeled results. Modeled pNH₄ is higher than data in the first two days (Fig. 10d). The measured NH₄ uptake rates after Day 2 are higher than modeled, again, likely due to the NH₄ substrate enhancement from ¹⁵N additions at low NH₄ concentrations. The modeled peak in pNO₃ at low NH₄ concentrations (Fig. 10d) was not observed in the data, where NO₃ uptake begins to increase in the last two days, as NO₃ concentrations in the enclosures begins to decrease. Some unknown factor appears to be selectively depressing NO₃ uptake in the Suisun Bay enclosure (Parker et al., 2012a). Trace metal leakage from paint from a large number of anchored naval ships (the U.S. Naval Reserve or “mothball fleet”) is one possibility (NOAA Office of Response and Restoration, 2009). Herbicides applied for agricultural weed control and marsh restoration are also sources of toxicity (Blaser et al., 2011; Blaser, 2012).

At Rio Vista, the disparity in NO₃ uptake between model output and measured data (Fig. 10f) is even more severe than in the Suisun Bay enclosure (Fig. 10d). NH₄ concentration drawdown is delayed until the end of the experiment, while modeled NH₄ concentration declines throughout the enclosure period and reaches zero after Day 3 enabling NO₃ decline (Fig. 10e). However, the data show no decline in NO₃ throughout the experiment. Measured pNO₃...
and $\rho$NH$_4$ (Fig. 10f) are nearly zero during the first two days and increase slightly toward the end of the time series. The expected peak in NO$_3$ uptake was not observed as NO$_3$ uptake rates remained almost zero throughout.

The patterns observed in the San Joaquin River enclosure (Fig. 10g) most resemble those of the Rio Vista enclosure, with slow NH$_4$ decline and no NO$_3$ drawdown (Fig. 10e) low uptake of NH$_4$ and virtually no NO$_3$ uptake (Fig. 10h) all in comparison with the modeled patterns. Comparison of these model simulations with enclosure data provides the basis for moving on to the next level of model with freshwater flow to simulate Suisun Bay.

4. Model runs with freshwater flow

4.1. Model runs with fixed flow, in fully mixed basin mode, with variable NH$_4$ inflow

The model was run at a fixed specific flow rate of 0.03 h$^{-1}$, essentially a dilution rate (Flow/Volume) and in this mode represents a hypothetical bay of 1 m$^3$ volume or any multiple thereof of keeping Flow/Volume = 0.03. The model was run with six NH$_4$ concentrations from 0.1 to 10 $\mu$mol L$^{-1}$; other parameters as in the non-flow model runs. After 240 h (10 days) the development of a phytoplankton bloom, simulated by turning on irradiance with a fully mixed water column and a uniform vertical light field is shown in Fig. 11a–d. The same basic sequence shown in the enclosure model runs and data occurs with a decline in NO$_3$ after a decline in NH$_4$ concentration to low, near zero values (Fig. 11a), NO$_3$ is drawn down to concentrations of 5–7 $\mu$mol L$^{-1}$ within 10 days, except at the highest NH$_4$ concentrations (5 and 10 $\mu$mol L$^{-1}$) when no drawdown occurs within the 10 day (240 h) period (Fig. 11a), a consequence of the continued elevated NH$_4$ concentrations at these two highest initial NH$_4$ inputs.

Specific NO$_3$ uptake, VNO$_3$, increases with elapsed time (Fig. 11b); however, the peak in VNO$_3$ is delayed at higher inflowing concentrations of NH$_4$ up to 1.5 $\mu$mol L$^{-1}$ and then VNO$_3$ falls to nearly zero at NH$_4$ concentrations of 5.0 $\mu$mol L$^{-1}$ and greater. VN$_H_4$ increases with greater inflowing concentrations of NH$_4$.
according to the Michaelis–Menten kinetics built into the model, but shows no increase with time and remains well below the peak values of VNO3 (Fig. 11b).

\( \rho \text{NO}_3 \) (Fig. 11c), follows closely that of VNO3 with peak values delayed and increasing as NH4 concentrations increase and falling to zero at initial NO3 concentrations of 5.0 µmol L\(^{-1}\) or greater. NH4 uptake (Fig. 11c) increases with time, even as the VNH4 declines, due to the increasing PON biomass. Increases in PON are delayed with increasing inflowing NH4 concentrations (Fig. 10d).

With inflowing NH4 up to 1 µmol L\(^{-1}\) a maximum biomass (as PON) of \( \approx 30 \) µmol L\(^{-1}\) is achieved after 10 days (240 h) and is based primarily on the assimilation of NO3 (Fig. 11d). At inflowing NH4 of \( \geq 5 \) µmol L\(^{-1}\) PON only reaches \( < 10 \) µmol L\(^{-1}\) (Fig. 11d). These plots show clearly the two states of a modeled bay phytoplankton-nitrogen ecosystem, with most inflowing NO3 exported unused when NH4 concentrations are higher, \( \geq 5 \) µmol L\(^{-1}\) (Fig. 11a).

Fig. 11d shows PON accumulation occurs when NO3 is accessed (Fig. 11c) and NH4 is low (i.e. NH4 < 1 µmol L\(^{-1}\)) in contrast to low PON accumulation with NH4 \( > 5 \) µmol L\(^{-1}\)). Intermediate conditions are described by the model with NH4 of 1 to 5 µmol L\(^{-1}\). PON produced from NH4 uptake increases with increased NH4 concentrations, but much less than the levels based on NO3. We ascribe this condition to the NH4 paradox (Dugdale et al., 2012). An illustration of how this can be extended to field conditions uses data from Central Bay (next to the Golden Gate). This SFE ecosystem in summer has an NH4 concentration of 5.3 µmol L\(^{-1}\) (Wilkerson et al., 2006). The model would predict the phytoplankton biomass as PON to be 7 µmol L\(^{-1}\), according to the NH4 curve for NH4(i) = 5 µmol L\(^{-1}\) in Fig. 11d. The average measured PON was 10.2 µmol L\(^{-1}\). This is the low PON accumulation state. As a consequence, even though NO3 concentrations are high in the summer in Central Bay (34.4 µmol L\(^{-1}\); Wilkerson et al., 2006) they are not used and the potential source of N for fueling productivity is exported to the ocean. Other estuaries with high NH4 inputs may exhibit this condition (i.e. unused NO3) predicted by the model.

4.2. Model runs with variable flow, in fully mixed basin mode, with fixed NH4 inflow concentrations

As flow is introduced into the model a boundary can be observed where the phytoplankton-nutrient system state drops into the NH4 based, low biomass, low productivity state (Fig. 12) at specific flows (i.e. flow normalized to the volume of a bay, i.e. \(= F/V \)) of 0.01–0.02 h\(^{-1}\) depending upon the initial NH4 conditions. The critical flow for a productivity system change is higher at lower NH4 concentrations. Above this critical flow rate, there is insufficient residence time available for the assimilation and reduction of NH4 to levels allowing phytoplankton NO3 uptake and PON accumulation.

4.3. Model runs with variable flow, fully mixed water column, with depth-integration allowing for light limitation

Model runs using estimates of depth-integrated NO3 and NH4 uptake were made at flows from 100 to 2000 m\(^{3}\)s\(^{-1}\) and inflowing concentrations of NH4 from 1 to 10 µmol L\(^{-1}\). Parameters were the same as in previous model run modes (Sections 4.1 and 4.2) however, NO3 and NH4 uptakes were estimated for the euphotic zone assuming that a single, light-saturated (i.e. 50% of surface irradiance) uptake rate was representative for the euphotic zone. The euphotic zone depth (1.05 m) was calculated from a mean Suisun Secchi depth of 0.3 m (Wilkerson et al., 2006) and the empirical relationship between Secchi depth and light attenuation coefficient as determined for Suisun Bay by Kimmerer et al. (2012). The euphotic zone N uptake was scaled to the ratio of the euphotic zone depth to the mean depth of Suisun Bay (5.61 m) and provided in these runs as depth-integrated N uptake values. Model runs were made for 30 days. Final values of PON are contoured in Fig. 13 on a NH4-flow plane. These contours show the two state ecosystem with a sharp transition from high, NO3 based productivity (i.e.

![Fig. 12. Model runs with varying flow, in fully mixed basin mode with fixed NH4 inflow concentrations. Effect of variable specific flow rate \((F/V, h^{-1})\) and initial NH4 of 5 or 10 µmol L\(^{-1}\) on the final PON concentration resulting after 240 h.](image)

![Fig. 13. Model runs with varying flow a fully mixed water column, with depth-integration allowing for light limitation. Effect of flow and initial NH4 concentrations on final PON concentrations (in µmol L\(^{-1}\) as contours with 30 µg L\(^{-1}\) in bold). Arrows show flows in dry, intermediate and wet water years from Peterson et al. (1985). Horizontal dashed lines plotted are mean NH4 concentrations (for spring 1970–1974 and 1999–2003) or criterion extended to the 30 µg L\(^{-1}\) contour and projected to the flow axis (x-axis). The Ball and Arthur (1979) vertical line is set at the maximum flow at which chlorophyll blooms were observed.](image)
high PON concentrations) to low, NH$_4$ based productivity (i.e. low phytoplankton biomass) delineated by the 30 µmol L$^{-1}$ PON contour. At high NH$_4$ concentrations (5–10 µmol L$^{-1}$) the contour lines are nearly vertical and small changes in flow result in a transition from one productivity state to the other. High NH$_4$ concentrations restrict the maximum flow to ~600 m$^3$s$^{-1}$ for high productivity. Changes in NH$_4$ concentration have far less effect than flow in this region. Below NH$_4$ of 5 µmol L$^{-1}$, the critical flow increases with decreasing NH$_4$ concentration to about 2 µmol L$^{-1}$ where the contours are horizontal and small changes in NH$_4$ concentration can result in a state transition; flow is less important than NH$_4$ in this region. In summary, low NH$_4$ concentrations allow higher flows for the high productivity (biomass) condition (up to 1500 m$^3$s$^{-1}$) and are more important than flow in this region for determining productivity condition.

5. Discussion

5.1. Comparison of no-flow model results with enclosure experiments

The model when run in the no-flow mode provides a diagnostic tool for interpretation of enclosure experimental data, offering mechanisms for phytoplankton and N interactions and suggesting next steps in understanding anomalous phytoplankton environmental conditions in the field. In some situations, modeled responses of NH$_4$ and NO$_3$ uptake and N drawdown agreed well with field data from a variety of enclosure experiments using water sampled from estuarine locations other than the location originally used to calibrate the model (i.e. Central Bay). In others, comparison of modeled results with data revealed conditions where patterns of phytoplankton uptake of NH$_4$ or NO$_3$ and biomass accumulation did not agree with the model. For example, the enclosures filled with water from Rio Vista (Fig. 10c) showed relatively slow NH$_4$ drawdown compared to modeled expectations, accompanied by delayed NO$_3$ drawdown, suggesting a growth-limited condition. These anomalous conditions that do not fit our modeled view of NH$_4$ and NO$_3$ interaction, are likely due to other parameters in the water, such as dominance by species other than diatoms and factors that directly affect N uptake and growth, e.g. herbicides (Blaser, 2012). Similar observations were made by Parker et al. (2012a,b) in experimental enclosures filled with water from a station in western Suisun Bay. The Suisun Bay enclosure (Fig. 10c) showed typical NH$_4$ drawdown but slow NO$_3$ drawdown compared to model results, suggesting a problem specific to NO$_3$ uptake, possibly unknown toxins affecting NO$_3$ transporters or the enzyme nitrate reductase. The usefulness of the model in these two cases is to provide suggestions for appropriate experiments, such as Toxicity Identification Evaluations (TIE’s) (e.g. US EPA, 1988) to isolate the specific problem causing the observed effects.

5.2. Comparison of with-flow model results with historical conditions

Phytoplankton blooms in Suisun Bay prior to 1987 were accompanied by complete drawdown of initial NH$_4$ and NO$_3$. Using data collected from 1969 to 1977 Ball and Arthur (1979) observed DIN to decline in the summer in Suisun Bay, to limiting concentrations, <0.02 mg N L$^{-1}$ (1.4 µmol L$^{-1}$) with peak summer concentrations of chlorophyll of 40–100 µg L$^{-1}$. Similarly, this was observed in Honker Bay (in Suisun Bay, Fig. 1) in 1970 by Di-Toro et al. (1977, their Fig. 13) who reported NH$_4$ concentrations to decline from 0.07 mg L$^{-1}$ (5.0 µmol L$^{-1}$) in May to undetectable in July and NO$_3$ from 0.4 mg L$^{-1}$ (28.6 µmol L$^{-1}$) to undetectable in July, when chlorophyll concentrations reached 50 µg L$^{-1}$. These pre-1987 blooms were supported by both NH$_4$ and NO$_3$ and were in the high biomass, NO$_3$ utilization state analogous to the high biomass state predicted by the SFE biogeochemical flow model, i.e. in the area of Fig. 13, to the left of the 30 µg L$^{-1}$ PON contour.

The mean spring NH$_4$ concentration for the years 1970–1974 (SUI spr. 1970–1974 in Fig. 13) in Suisun Bay (Station D6) of 4.95 ± 1.49 µmol L$^{-1}$ (Ball, 1977) is plotted on the y-axis of Fig. 13. A horizontal line drawn from this NH$_4$ concentration intersects the 30 µg L$^{-1}$ PON contour at a flow rate of ~700 m$^3$s$^{-1}$ (vertical line drawn to the x-axis), setting the maximum flow rate that would allow a high biomass bloom to occur. Ball and Arthur (1979) considered the Suisun Bay phytoplankton standing crop before 1976 to be related directly to water transparency and indirectly to Delta outflow (i.e. river flow) and concluded that only when the outflow varied between 110 and 700 m$^3$s$^{-1}$ did chlorophyll concentrations of >20 µg L$^{-1}$ occur in the entrainment zone adjacent to the shallows of Suisun/Honker Bay, the same maximum flow predicted by the model for the mean NH$_4$ concentration.

5.3. Comparison of with-flow model results with contemporary conditions

More recently (1999–2003) the mean spring NH$_4$ concentration in Suisun Bay was 6.8 µmol L$^{-1}$ (Wilkerson et al., 2006) which intersects the 30 µmol L$^{-1}$ PON contour near 600 m$^3$s$^{-1}$ (Fig. 13), setting an upper flow limit for high biomass accumulation slightly lower than the prediction from the pre-1987 data (~700 m$^3$s$^{-1}$). Another prediction of the maximum flow rate for bloom formation is obtained by plotting the 4 µmol L$^{-1}$ NH$_4$ concentration criterion below which NO$_3$ uptake occurs and bloom formation begins (Dugdale et al., 2012) on the y-axis of Fig. 13, yielding a maximum flow rate of just over 800 m$^3$s$^{-1}$.

Over the range of NH$_4$ concentrations from 4.0 to 6.8 µmol L$^{-1}$, predicted maximum river flow rates range narrowly from 600 to 800 m$^3$s$^{-1}$ in good agreement with the maximum river flow, 700 m$^3$s$^{-1}$, suggested by Ball and Arthur (1979). Two large blooms were observed in Suisun Bay from mid-April to the end of May 2010. The mean Delta Outflow during that period was 644.5 ± 113.9 m$^3$s$^{-1}$ just below the maximum flow (700 m$^3$s$^{-1}$) described by Ball and Arthur (1979), and also below the modeled estimate of maximum flow (800 m$^3$s$^{-1}$) for the 4 µmol L$^{-1}$ NH$_4$ concentration criterion. The mean Delta Outflow 2010 flow during the bloom period was also below the washout flow criterion of 1100 m$^3$s$^{-1}$ calculated by Dugdale et al. (2012), above which phytoplankton populations are washed out and cannot bloom. This washout criterion is based on the mean spring NH$_4$ uptake rate of the phytoplankton in Suisun Bay (Dugdale et al., 2012) and above that flow rate, the growth rate of the phytoplankton is less than the loss rate due to flow and the population is washed out and shows zero growth or net loss.

In addition to NH$_4$ and flow impacts on phytoplankton blooms, grazing by invasive clams (Potamocorbula amurensis) could contribute to declining chlorophyll concentrations and lack of spring blooms although clams are in low concentration and size in spring (Greene et al., 2011). However, as discussed in Dugdale et al. (2012) clam abundance in Suisun Bay was unchanged in spring 2010, when there was a phytoplankton bloom, and were monitored at similar densities to previous years (in spring) when blooms were absent.

5.4. Comparison of with-flow model results with wet versus dry years

The mean river freshwater flows in spring for wet, intermediate and dry years (Peterson et al., 1985) are shown as arrow heads drawn on the x-axis. The model in its present form suggests that dry and intermediate years should allow phytoplankton blooms
(i.e. PON > 30 μmol L⁻¹, equivalent to chl > 30 μg L⁻¹; Dugdale et al., 2012) at NH₄ concentrations up to 10 μmol L⁻¹. However, in wet years, NH₄ concentrations would have to be ≤ 4 μmol L⁻¹ for blooms to occur.

5.5. Model predictions of spring bloom occurrences in Suisun Bay

The similarity in freshwater flow relationship to phytoplankton blooms in Suisun Bay in the 1970s and recently in 2010, leads to the suggestion that the mechanism behind the earlier blooms was essentially the same as presently observed in Suisun Bay when NH₄ concentrations are low (Wilkerson et al., 2006; Dugdale et al., 2007, 2012). This mechanism requires that phytoplankton be able to access the available NO₃ for growth which does not happen when NH₄ concentrations are high. The with-flow model results are consistent with this view. The model results are also consistent with the conclusion of Jassby (2008) that biomass accumulation is inversely related to freshwater flow, a consequence of reduced residence time with increased flow.

However, the model predicts high biomass with any concentration of NH₄ up to 10 μmol L⁻¹ and flows of less than 500 m² s⁻¹ (intersection of 10 μmol L⁻¹ NH₄ with the 30 μg L⁻¹ PON). Typically low flows would be expected in the summer. However, high levels of biomass do not occur in summer and have only been observed rarely in spring (i.e. Wilkerson et al., 2006; Dugdale et al., 2012). In the model any factor that reduces the rate at which NH₄ concentrations decline or that add to the NH₄ concentration will extend the period without NO₃ uptake and prevent biomass accumulation. High rates of benthic regeneration of NH₄, unaccounted-for sources of NH₄ (e.g. waste water treatment plants) and high grazing rates by either benthos or zooplankton would have such an effect. None of these possibilities are considered in the present model. Clam biomass and grazing is highly seasonal and may be the most likely source of regenerated nitrogen as NH₄ in summer and fall.

The model could be expanded in several ways. Both clam and zooplankton grazing could be added to the model in the near future. Exchange of NH₄ with the sediment has been measured in Suisun Bay (J. Cornwell, personal communication) at rates that suggest it will be necessary to include this source/sink in the model. Pelagic nitrification (NH₄ oxidation to NO₂⁻) by bacteria and archaea has been estimated to be greater than phytoplankton NH₄ uptake in the Sacramento River (Parker et al., 2012a,b) and consumes oxidation in the process of producing NO₃. A nitration pathway needs to be included in a future model. Then rates of nitrification measured with ¹⁵N (Parker, personal communication) should be compared to the model estimates. These enhancements to the model would provide a more complete description of the pattern of NH₄ fluxes and concentrations with time. Other phytoplankton functional groups such as cyanobacteria could also be added. Ongoing studies of the effect of NH₄ concentration and N:P ratio will provide data for validation of the enhanced model. Toxicity of NH₄ to diatoms has not been included in the current model. However, NH₄ inhibition of NH₄ uptake by phytoplankton has been shown to occur in the Sacramento River when NH₄ concentrations are >20 μmol L⁻¹. Such high concentrations of NH₄ have not been observed in the source waters to Suisun Bay. To make the model functional for the Sacramento River such an inhibition term could be added.

5.6. Future uses for the model

The model results suggest that reduction in inflowing NH₄ concentrations to Suisun Bay would reduce or eliminate the NH₄ sensitivity of phytoplankton biogeochemical processes in the Bay. With these NH₄ reductions, spring phytoplankton bloom occurrence would be dependent upon freshwater flow conditions, strongly improving the likelihood of blooms and food supply to pelagic organism decline species. On the other hand, proposed increases in freshwater flow, to provide more suitable habitat for the delta smelt, would be predicted to have no significant effect on phytoplankton productivity if NH₄ concentrations were low, but could quite drastically reduce the biomass of phytoplankton at the present mean NH₄ concentrations (e.g. 6.8 μmol L⁻¹ in Suisun Bay) (Fig. 13).

The present model is one dimensional and nitrogen-based, and at this point should be regarded as a step in the development of a full three dimensional model of the SFE/Delta system. This tool will help elucidate the pre-1987 ecosystem processes and the parameters of management and regulatory strategies. A unique aspect of the present model is the inclusion of terms for the time varying rate of maximum NO₃ uptake as a function of NO₃ concentration (acceleration) and for inhibition of NO₃ uptake by NH₄. The model of Di-Torro et al. (1977) included a mechanism for considering preferential use of NH₄ and NO₃ uptake by estuarine phytoplankton, ensuring that NH₄ is used before NO₃. However, the likely role of NH₄ in creating a stable two-state productivity (biomass) ecosystem and elucidating the flow–bloom pattern in Suisun Bay has not been considered before. The modeled phytoplankton biomass in the two states of Suisun Bay may be analogous to previously existing ecosystem states of the SFE described by Gilbert et al. (2011). The modeled high biomass, NO₃ based, high productivity state would be analogous to the pre-1982, diatom era with large copepods (Eurytemora) and delta smelt (Gilbert et al., 2011). The modeled low biomass, low productivity state based on NH₄ would be analogous to the post 1982 cryptophyte/flagellate era with small copepods (Pseudodiaptomus) with bass and shad. Gilbert et al. (2011) attribute the change in food web components to the shift in the dominant form of DIN, NH₄ becoming more dominant post 1982.

The model can be improved and extended with the addition of grazing terms, and chemical transformations (e.g. nitrification) as discussed. Such an improved version of this relatively simple, validated model could be embedded into three dimensional biogeochemical models under construction for the SFE and Delta (Chai, Chao and Atelejevic, personal communication) to aid in management of freshwater flows, nutrients and fishery problems. Ongoing field and laboratory studies will provide ample data for validation of such additions to the model. The basic model (without flow) can be used to interpret nutrient/phytoplankton interactions in experimental mesocosms. The biogeochemical model (in the mode with flow) is easy to initiate and can be applied to other urban estuaries with anthropogenic nutrient loading and freshwater flow concerns and be used to test possible management scenarios.

Acknowledgments

This material is based upon work supported by the Delta Stewardship Council under Grant No. 1039. Enclosure experiments conducted in the Sacramento River were funded by the Federal and California State Water Contractors, the San Luis and Delta-Mendota Water Authority and California Regional Water Quality Control Board Region 5. We wish to thank Drs Fei Chai and Steve Culberson for critical reading of the manuscript.

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