Available online at www.sciencedirect.com
ScienceDirect
Estuarine, Coastal and Shelf Science 73 (2007) 17–29
ESTUARINE COASTAL AND SHELF SCIENCE
www.elsevier.com/locate/ecss

The role of ammonium and nitrate in spring bloom development in San Francisco Bay

Richard C. Dugdale*, Frances P. Wilkerson, Victoria E. Hogue, Albert Marchi

Romberg Tiburon Center, San Francisco State University, 3152 Paradise Drive, Tiburon, CA 94920, USA

Received 19 April 2006; accepted 13 December 2006
Available online 2 February 2007

Abstract

The substantial inventory of nitrate (NO_3) in San Francisco Bay (SFB) is unavailable to the resident phytoplankton most of the year due to the presence of ammonium (NH_4) at inhibitory concentrations that prevents NO_3 uptake. Low annual primary productivity in this turbid estuary is generally attributed to the poor irradiance conditions. However, this may not be the only cause; spring phytoplankton blooms occur irregularly in north SFB only when NH_4 concentrations are low, <4 μmol L^{-1} and NO_3 uptake by phytoplankton occurs. Field measurements and enclosure experiments confirm the NH_4 inhibition process to be the cause of low NO_3 utilization most of the year. Detailed analysis of spring blooms in three embayments of SFB over 3 years shows a consistent sequence of events that result in bursts of chlorophyll. The first requirement is improved irradiance conditions through stabilization of the water column by stratification or reduced tidal activity. Second, NH_4 concentrations must be reduced to a critical range, 1 to 4 μmol L^{-1} through dilution by precipitation and by phytoplankton uptake. This enables rapid uptake of NO_3 and subsequent increase in chlorophyll. The resulting bloom is due to both the initial uptake of NH_4 and the subsequent uptake of NO_3. The NO_3 uptake step is crucial since it is the larger nitrogen source and uptake occurs at higher rates than that for NH_4 at the concentrations that occur in SFB. Existing models of light-limited, non-nutrient limited productivity in SFB require modification to include the NH_4 inhibition effect. From measured NH_4 uptake rates and initial concentrations, calculations can be made to predict the length of time that favorable irradiance conditions are required for the phytoplankton population to reduce ambient NH_4 concentrations to non-inhibiting concentrations and allow bloom formation to begin. For Suisun Bay, the time required is so long that blooms are unlikely in any season. For San Pablo and Central Bays, these times are too long in summer but sufficiently short in spring to allow bloom development, depending on the ambient NH_4 concentration prior to the productivity season. NH_4 sources to SFB are primarily anthropogenic, from agricultural drainage and sewage treatment plants, and if not sufficiently diluted by runoff and precipitation can prevent development of the spring phytoplankton bloom. Attention should be paid to the form of N making up dissolved inorganic nitrogen (DIN) in nutrient-rich estuaries.

Keywords: phytoplankton; estuary; ammonium; nitrate

Regional index terms: California; San Francisco Bay

1. Introduction

Turbid estuaries often exhibit low primary production that is usually attributed to the poor irradiance conditions and a shallow euphotic zone (Cloern, 1987). However, even in these estuaries, considerable variability in primary productivity may occur over a variety of time scales, from daily to interannual. The timing and number of productivity events that occur in any one season are likely to play important roles in the provisioning of the food chain. Especially important may be the disruption of normal ecosystem cycles. For example, zooplankton species evolved to depend on phytoplankton blooms in spring for food and egg production, may find the expected bloom to be absent or moved significantly in time from the normal seasonal cycle. Changes in turbidity cycles, e.g. changes in

* Corresponding author.
E-mail addresses: rdugdale@sfsu.edu (R.C. Dugdale), fwilkers@sfsu.edu (F.P. Wilkerson), vhogue@sfsu.edu (V.E. Hogue), amarchi@sfsu.edu (A. Marchi).

0272-7714/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ecss.2006.12.008

flow and wind patterns clearly have the potential for disrupting productivity cycles in turbid estuaries. However, other factors may be important as well in influencing timing and magnitude of primary production. Here, we consider the role of two different forms of inorganic nitrogen in modifying classical spring blooms of phytoplankton in San Francisco Bay (SFB), a turbid estuary impacted by anthropogenic inputs of nitrogenous nutrients (Schemel and Hager, 1986). Conventional wisdom suggests that NH_4 and NO_3 loadings to an estuary can be combined together as dissolved inorganic nitrogen (DIN) since phytoplankton have been shown in culture to grow equally well on both nitrogen sources (Syrett, 1981). Phytoplankton are also thought to prefer NH_4 as a nitrogen source since the energetic costs of assimilating that species of nitrogen are less than that for NO_3. By inference, an estuary whose phytoplankton are utilizing NH_4 for growth should have the same primary productivity as if they were using NO_3, or perhaps even higher productivity on NH_4 compared to NO_3.

The ability to separate out the use of NO_3 and NH_4 by phytoplankton in the marine environment was pioneered by Dugdale and Goering (1967) using the stable isotope ^{15}N as a tracer. This has proved to be a powerful tool in studies of primary production in marine ecosystems. In productive oceanic ecosystems, the most abundant species of DIN is NO_3 since NH_4 is readily oxidized to NO_3 and is the minor inorganic species (Codispoti, 1985). Although under some culture conditions algae use both forms of DIN simultaneously (Dortch, 1990), NO_3 uptake is suppressed or inhibited by relatively low concentrations of NH_4 as shown, for example, by Conway (1977) for the diatom *Skeletonema costatum* and by Cochlan and Harrison (1991) for the picoplankton species *Micromonas pusilla*. Field studies using ^{15}N have confirmed the relationship between elevated NH_4 concentrations and low NO_3 uptake rates, e.g. in the Saronikos Gulf (Greece) due to the effects of sewage inputs (Dugdale and Hopkins, 1978); the Peru coastal upwelling system (Dugdale and MacIsaac, 1971); and more recently the upwelling center off Bodega Bay, California (Dugdale et al., 2006). In each of these studies, NO_3 uptake was negatively correlated and reduced to low levels with ambient NH_4 concentrations in the range of 1–2.5 $\mu mol\,L^{-1}$. ^{15}N studies in a series of upwelling sites, from Baja California to northwest Africa and Peru showed maximum specific NO_3 uptake rates to always exceed maximum specific NH_4 uptake rates with the conclusion "that the high biological productivity of the Peruvian upwelling system may be linked to the ability of the phytoplankton to take up and utilize NO_3 at an extraordinary rate" (Codispoti et al., 1982). By analogy with these marine studies, estuaries could be expected to have higher primary productivity with phytoplankton growing on NO_3 than when growing on NH_4. However, if NH_4 is at an inhibitory level, this form of DIN may not allow the high NO_3-based productivity. San Francisco Bay, as an urban estuary impacted by anthropogenic inputs and with the likelihood of high NH_4 concentrations, provided an ideal environment to investigate this scenario.

We initiated studies of nutrient and productivity processes in SFB in 1997 using the stable isotope tracer ^{15}N and found that NH_4 uptake by phytoplankton in Central SFB dominated DIN uptake and that NO_3 uptake was a rare occurrence in spite of abundant ambient NO_3 concentrations (Hogue et al., 2005). Similar observations were made for the Delaware Estuary (Pennock, 1987) where NH_4 fuels productivity in a high NO_3 setting. Most annual primary production in central SFB depended upon NH_4 (Hogue et al., 2005) except during spring when ambient NH_4 concentrations fell to low values and high levels of primary production based on NO_3 occurred. Subsequent measurements in the northern estuary (Suisun, San Pablo and Central Bays) were carried out from 1999 to 2002 that described the seasonal variability in nutrients, nutrient uptake and phytoplankton abundance (Wilkerson et al., 2006). In fall, there were small occasional blooms fueled by NH_4 uptake by small-sized phytoplankton but the major periods of high productivity and chlorophyll accumulation occurred in spring dominated by large-sized phytoplankton, mostly diatoms (Cloern and Dufford, 2005). During spring blooms, there were higher rates of NO_3 uptake than NH_4 uptake indicating higher growth rates on NO_3 by the phytoplankton. Spring blooms were observed in all three bays in 2000, but only in San Pablo and Central Bays in 2001 and 2002. Interestingly, the bloom in Suisun Bay in spring 2000 had the greatest phytoplankton abundance observed reaching 30 $\mu g\,L^{-1}$ chlorophyll. This occurred when there were very low salinity values and low NH_4 concentrations, neither of which occurred there in 2001 or 2002 (Wilkerson et al., 2006), accompanied by high NO_3 uptake rates. This suggested that NH_4 played a role in bloom dynamics, by limiting phytoplankton access to the NO_3 pool. The goal of this study was to analyze the data collected during the 1999–2002 study and to use experimental enclosures to determine the conditions and mechanisms required to give phytoplankton access to the ambient NO_3 and accumulate chlorophyll during spring blooms. We evaluate the role of two components of the DIN pool (i.e. NH_4 and NO_3) and their interaction as modulators of the development and/or suppression of spring blooms in San Francisco Bay.

2. Methods

2.1. Field data

Cruises designed to sample San Francisco Bay (SFB) monthly and weekly during the spring months of March and April were conducted aboard the R/V Questuary from November 1999 to August 2003. Water was sampled at three locations: Suisun Bay (USGS Sampling Station 6, 38′ 3.9°N 122′ 2.1°W), San Pablo Bay (USGS Station 13, 38′ 1.7°N 121′ 22.2°W) and Central Bay (RTC Station XB-D, 37′ 53.83°N 122′ 25.5°W) using a Seabird SBE-19 CTD and 3-L Niskin bottles mounted on an SBE-33 carousel. Surface samples were taken for analyses of nutrients, chlorophyll *a* and ^{15}N labeled NO_3 or NH_4 uptake. The complete time series data (temperature, salinity, nutrients and size fractionated biomass and DIN uptake) are described in Wilkerson et al. (2006).

2.2. Enclosure experiments

The progression of DIN uptake was investigated in SFB water containing different ambient levels of NH_4 or treated with different additions of NH_4. In 1999, six experiments (labeled A–F) were carried out on different days in April to July (Hogue, 2000) using 1-L polycarbonate bottles filled with surface water from Central Bay sampled between the high and low afternoon tides. The experiments (A–F) started with different ambient NH_4 concentrations. In April 2003, an enclosure experiment was conducted in which additions of NH_4 (5 to 30 μmol L^{-1} of NH_4Cl) were made to surface Central Bay water placed in 20-L polyethylene cubitainers. All enclosures were placed in water-cooled tables under mesh screening (to reduce light to 50% of ambient available light). The enclosures were sampled daily for up to 4 days for nutrients, chlorophyll *a* and uptake of $^{15}NO_3$ or $^{15}NH_4$.

2.3. Analytical methods

NO_3 concentrations were determined using a Bran and Lubbe AutoAnalyzer II (Whitledge et al., 1981) and NH_4 using a spectrophotometer according to Solorzano (1969). Water samples were prefiltered using precombusted GF/F filters before NH_4 analysis. Chlorophyll *a* was determined by in vitro fluorometry (Arar and Collins, 1992) using a Turner Designs Model 10 fluorometer, calibrated with commercially available chlorophyll *a* (either Sigma Chemical Company or Turner Designs) on samples filtered onto Whatman 25 mm GF/F filters. Nitrogen uptake was measured using ^{15}N additions to SFB water or water sampled from enclosures and the ^{15}N incorporated measured using mass spectrometry. Uptake incubations were carried out in 280-ml polycarbonate bottles, for 24 h (for time series data, Wilkerson et al., 2006) or 6 h around local noon (for the enclosure data) on incubation tables cooled with filtered SFB water and under screening to expose them to 50% of ambient light. ^{15}N inoculations were of trace additions (approximately 10% of ambient DIN concentrations) or saturated (5 μmol L^{-1}) additions of either $K^{15}NO_3$ or $^{15}NH_4Cl$ (99 atom% ^{15}N). Cases where saturated additions were used are noted in the figure legends. Incubations were terminated by filtration onto precombusted (450 °C for 4 h) 25 mm GF/F filters and frozen until analysis for ^{15}N enrichment with a Europa Tracermass (Wilkerson and Dugdale, 1992) or PDZ 20/20 mass spectrometer system. The transport rates (ρ, in μmol L^{-1} h^{-1}) and V (biomass specific uptake in h^{-1}) were calculated according to Dugdale and Wilkerson (1986).

3. Results

3.1. Field data from Suisun, San Pablo, and Central Bays

To establish the role of DIN and interacting nutrient processes in occurrences and extent of SFB blooms, the time series data for concentrations of chlorophyll, NH_4, and NO_3 and uptake of $^{15}NO_3$ in Suisun, San Pablo, and Central Bays, measured between late 1999 and 2003 are shown in Fig. 1a–d. Four spring peaks in chlorophyll (blooms) occur in San Pablo and Central Bays (Fig. 1a) that coincide with reduced NH_4 concentrations, often near zero (Fig. 1b). In Suisun Bay, only one bloom was observed, in 2000 that occurred when NH_4 concentrations were low in the spring, in contrast to the other years when NH_4 levels were high. The chlorophyll peaks in all bays were coincident with peaks in $^{15}NO_3$ uptake (Fig. 1c) that was otherwise very low (almost zero) the rest of the time. In all three bays sampled, concentrations of NH_4 were above 4 μmol L^{-1} most of the year (Fig. 1b), except during the spring bloom periods. Nitrate was high (non-limiting), >20 μmol L^{-1} most of the year (Fig. 1d). Winter uptake rates were lowest of all seasons probably due to poor irradiance conditions.

When all the $^{15}NO_3$ uptake rates collected from the three bays are plotted versus NH_4 concentration (Fig. 2a), a distinct threshold is seen such that very low NO_3 uptake occurs at higher NH_4 concentrations (>4 μmol L^{-1}). The ratio of ρNO_3 to ρNH_4 uptake shows the same trend with low ratios at high NH_4 concentrations (Fig. 2b). The symbols used for these ratios are bubbles that reflect the chlorophyll concentration. With low NH_4 concentrations (i.e. <4 μmol L^{-1}), there are higher ratios of ρNO_3 to ρNH_4 and larger chlorophyll biomass (bigger bubbles) (Fig. 2b). Together these two figures (Fig. 2a,b) and the time series plots (Fig. 1) show that "bloom" levels of chlorophyll are evident only when NO_3 uptake occurs and that NO_3 uptake only takes place at lower ambient NH_4 concentrations.

To observe this relationship during just the spring bloom periods, biomass specific nitrate uptake rates, VNO_3 versus ambient NH_4, were plotted for all three bays using data only from the spring seasons (Fig. 3). These also show a pattern of rapidly rising values of VNO_3 at NH_4 concentrations below about 4 μmol L^{-1} NH_4 likely caused by NH_4 inhibition of NO_3 uptake. A variety of mathematical formulations of NO_3 uptake inhibition by NH_4 have been described including both linear and exponential (Dortch, 1990). Cochlan and Harrison (1991) fitted experimental data of NH_4 inhibition of NO_3 uptake from cultured phytoplankton with an exponential function. The best fit to the SFB spring data set for San Pablo and Central Bays was obtained with a power exponential function, $\ln VNO_3 = -1.28 \times \ln [NH_4] - 4.26$ (Fig. 3). Although the r^2 was fairly low (0.5), the visual fit and the curvilinear exponential agreement with the Cochlan and Harrison (1991) relationship suggest that the field data showing low NO_3 uptake at elevated NH_4 concentrations are consistent with interpretation as the result of NH_4 inhibition.

When NH_4 uptake is plotted versus NH_4 for San Pablo and Central Bays using spring data (Fig. 4a), a pattern opposite to that of VNO_3 results, i.e. decreasing VNH_4 with decreasing NH_4 concentrations, that can be fit with a straight line ($VNH_4 = 0.025 \times [NH_4]$) with an r^2 of 0.9. The relationship for VNH_4 versus NH_4 for Suisun Bay shows no obvious pattern (Fig. 4b), which cannot be explained at present but has been observed in samples since 2002 and in recent enclosure

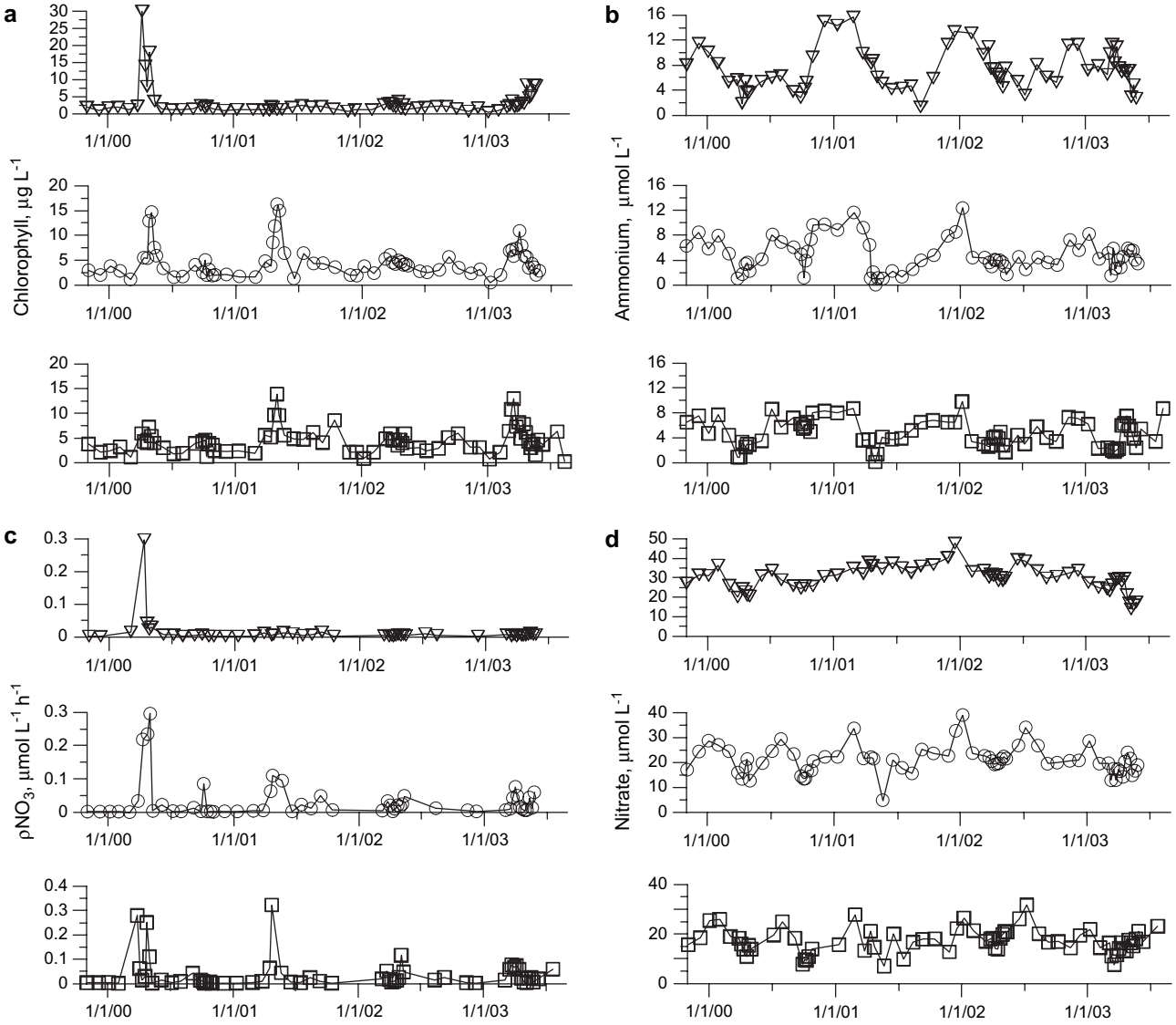


Fig. 1. Surface time series data collected in Suisun (triangles), San Pablo (circles) and Central Bays (squares) from November 1999 to August 2003. (a) Chlorophyll *a*, µg L^{-1}, (b) NH_4, µmol L^{-1}, (c) trace $\rho^{15}NO_3$, µmol L^{-1} h^{-1}, (d) NO_3, µmol L^{-1}.

experiments using water from all three bays. Suisun Bay enclosures show consistently low initial NH_4 uptake rates (A. Parker, pers. comm.). Figs. 3 and 4 imply that with decreasing NH_4 concentrations, if NO_3 is present, a transition from primarily NH_4-based N uptake (Fig. 4a) to primarily NO_3 uptake will begin at about 4 µmol L^{-1} NH_4 increasing rapidly by 1 µmol L^{-1} where inhibition has decreased to 60% (calculated from the exponential fit in Fig. 3) and will end with solely NO_3 uptake (Fig. 3) when NH_4 concentration is reduced to zero.

3.2. Bloom development in San Pablo Bay, Spring 2001 and Central Bay, Spring 2002

To examine the transition between predominantly NH_4 uptake and predominantly NO_3 uptake and the consequences on algal biomass accumulation as chlorophyll in SFB, rates during the spring blooms of 2001 in San Pablo and 2002 in Central Bay were studied in more detail. The sequence of events in San Pablo Bay leading to the 2001 phytoplankton bloom began in late February with NO_3 concentrations >20 µmol L^{-1} (Fig. 1d), NH_4 concentrations >10 µmol L^{-1} and low specific N uptake rates, VNH_4 and VNO_3, <0.005 h^{-1} (Fig. 5a). Chlorophyll was also low, <2 µg L^{-1} as were ρNH_4 and ρNO_3, <0.02 µmol L^{-1} h^{-1} (Fig. 5b). March samples were characterized by an increase in VNH_4 (Fig. 5a), but no increase in VNO_3, an increase in ρNH_4, but not in ρNO_3, (Fig. 5b), an increase in chlorophyll (Fig. 5b) and a decrease in NH_4 (Fig. 5a). By mid-April, NH_4 concentration fell to ca. <2 µmol L^{-1}, VNH_4 and ρNH_4 decreased to low, February values. However, VNO_3 increased as did ρNO_3 along with chlorophyll concentration that all rose steeply reaching maxima at the time when the sum of ρNH_4 and ρNO_3 reached a peak (Fig. 5b). Following the peak in chlorophyll, NO_3 concentration fell to ca. 5 µmol L^{-1} (not shown), VNO_3 and ρNO_3 decreased to reach February values by early June and chlorophyll declined, marking the end of the spring bloom. This same temporal

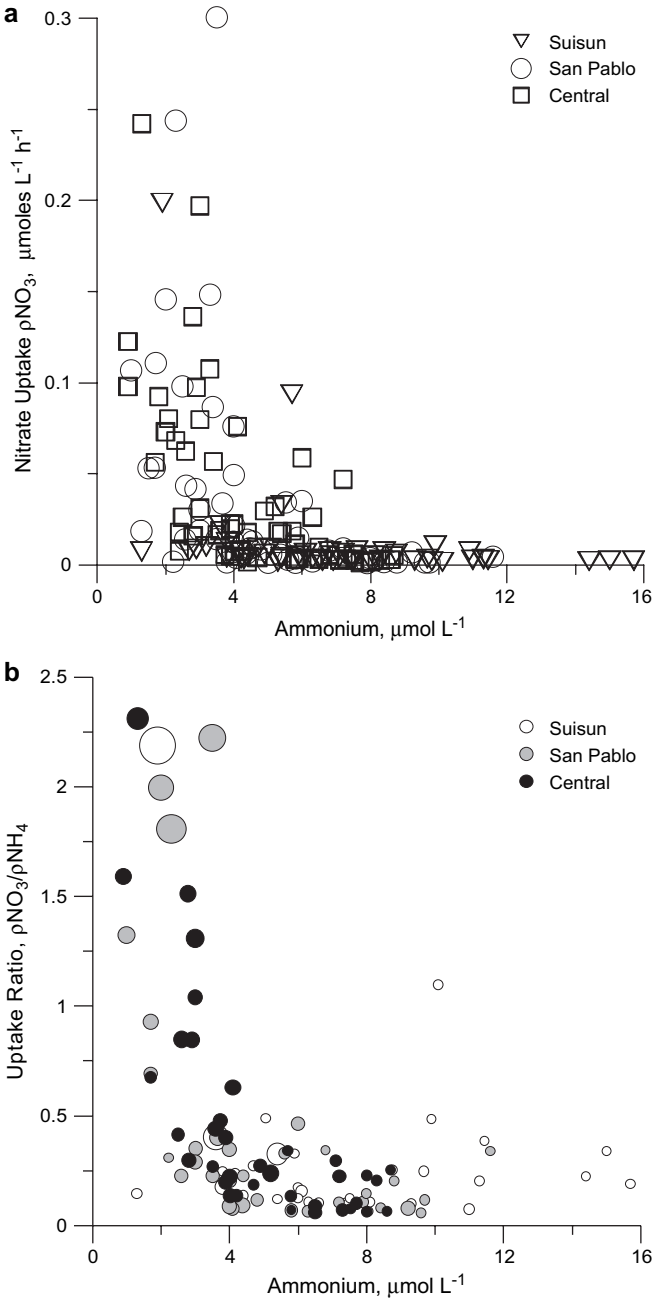


Fig. 2. (a) Saturated ρNO_3, $\mu mol\,L^{-1}\,h^{-1}$ versus NH_4, $\mu mol\,L^{-1}$ for Suisun, San Pablo and Central Bays and (b) ratio of saturated ρNO_3 to ρNH_4 versus NH_4, $\mu mol\,L^{-1}$. The points in the graph are shown as bubbles that indicate chlorophyll concentration.

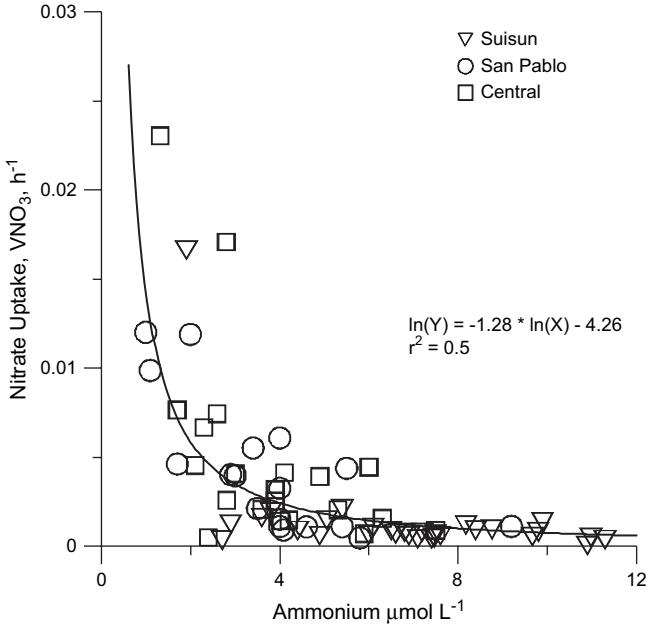


Fig. 3. Trace VNO_3, h^{-1} versus NH_4 concentration, $\mu mol\,L^{-1}$ for the spring bloom periods in Suisun, San Pablo and Central Bays. Exponential line fit through the San Pablo and Central Bay data.

sequence resolved on a better time scale (as weekly samples were available), with rising VNH_4, falling NH_4 concentration, rising VNO_3, and peak values of combined NH_4 and NO_3 uptake and chlorophyll concentration occurred in the Central Bay during development of the spring bloom in 2002 (Fig. 6a,b).

These trends can be interpreted as the result of the following physiological response sequence to initially non-limiting levels of NH_4 and NO_3: (1) an increase in VNH_4 (presumably the result of improved irradiance/stability conditions) resulting in a small increase in biomass (chlorophyll); (2) as a result of the increase in p NH_4 (i.e. $VNH_4 \times$ biomass as particulate nitrogen, PON), a decrease in NH_4 concentration occurs to less inhibiting levels for NO_3 uptake; and then (3) VNO_3 rises and with an increase in ρNO_3 fuels a strong increase in biomass. Although VNH_4 has declined to low levels at this stage, ρNH_4 remains relatively high due to the high biomass (i.e. low $VNH_4 \times$ high PON = high ρNH_4). Then (4) a short period of high ρN_{total} (i.e. sum of ρNO_3 and ρNH_4) occurs as chlorophyll concentration peaks; and (5) finally reduced ambient concentrations of NO_3 and NH_4, no longer support the phytoplankton population and the spring bloom is terminated. There are two transition points or ''thresholds'' for NH_4 concentration that need to be distinguished and kept in mind. The first is the 4 $\mu mol\,L^{-1}$ value when chlorophyll accumulation based on NH_4 uptake begins, and the second, about 1 $\mu mol\,L^{-1}$ NH_4 when the inhibition effect is reduced to about half maximum (60% according to the curve fit in Fig. 3). Below that value NO_3 uptake increases steeply with decreased NH_4 concentrations. Neither of these values should be taken as invariant, but in SFB they are in the expected order, NH_4 uptake first, then NO_3. With favorable irradiance and water column stability, the signature of an oncoming spring bloom is the simultaneous decline in VNH_4 and increase in VNO_3 and a maximum in summed NH_4 and NO_3 uptake coinciding with a peak value of chlorophyll. This sequence explains the apparent requirement for NO_3 uptake for bloom formation, the threshold of ca. 4 $\mu mol\,L^{-1}$ NH_4 below which high chlorophyll concentrations develop, and the high ratio of NO_3 to NH_4 uptake (>1) when chlorophyll concentrations are high (Fig. 2b).

3.3. Enclosure experiments

A series of mesocosm/enclosure experiments were conducted using SFB water to track phytoplankton uptake rates

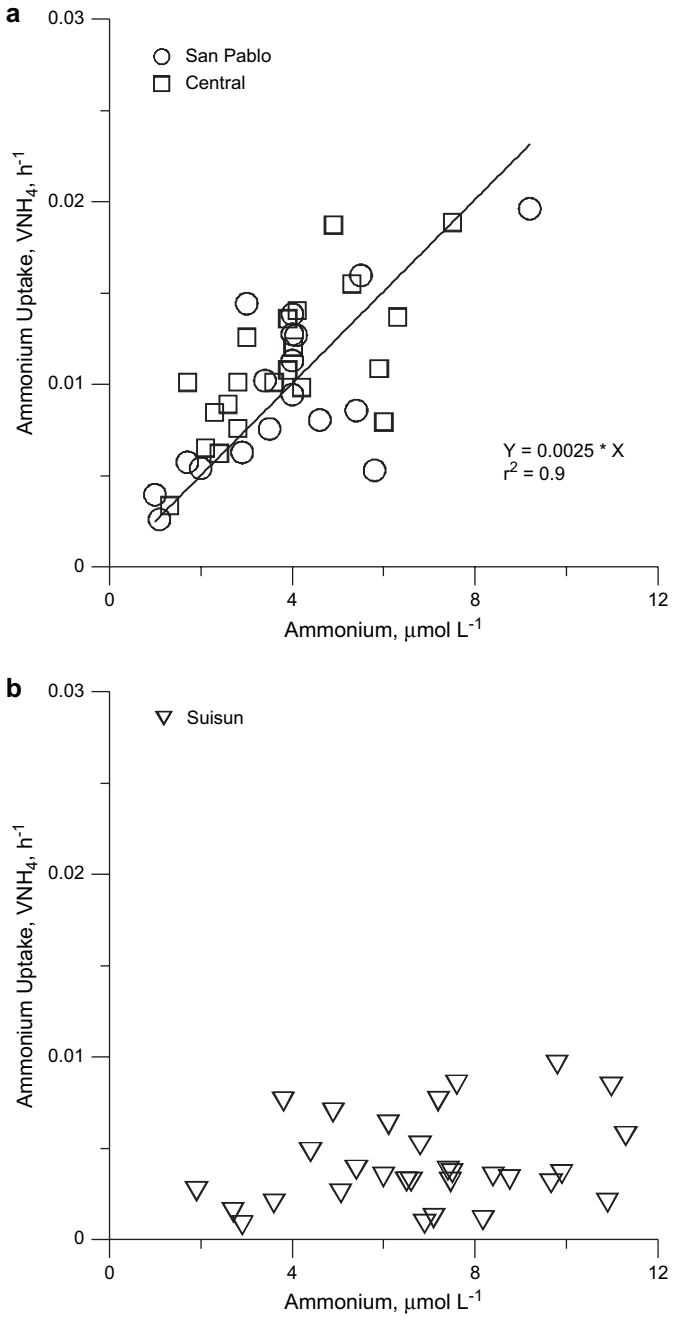


Fig. 4. Trace $V\mathrm{NH_4}$, $\mathrm{h^{-1}}$ versus $\mathrm{NH_4}$ concentration, $\mu\mathrm{mol\,L^{-1}}$ for the spring bloom periods in (a) San Pablo and Central Bays, (b) Suisun Bay.

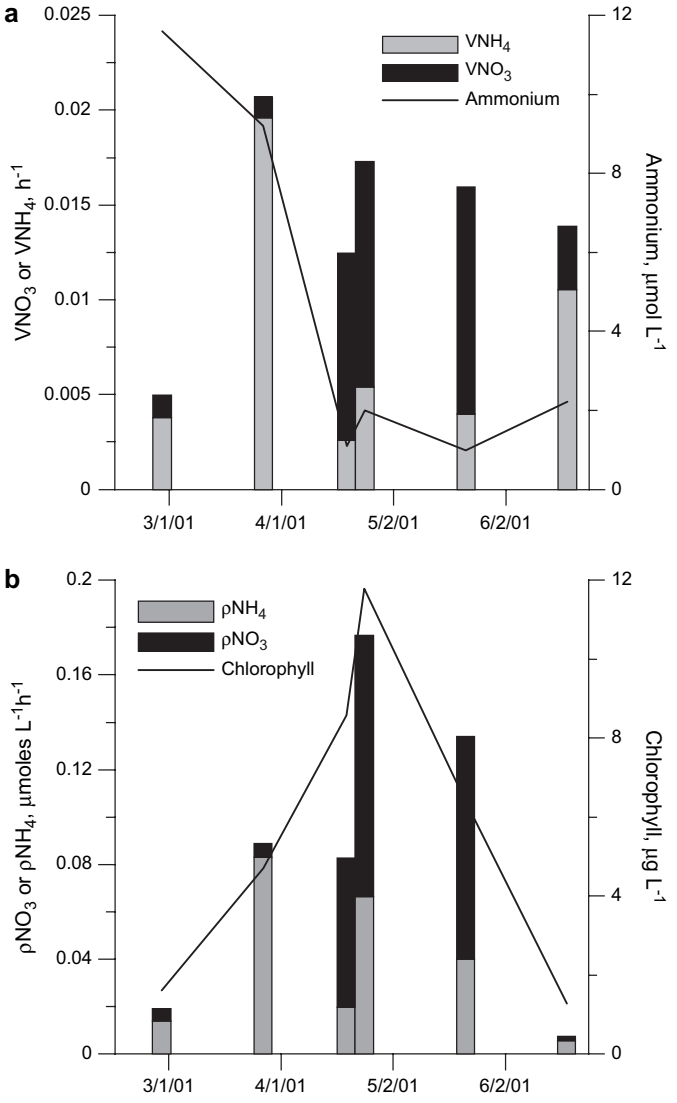


Fig. 5. (a) Trace $V\mathrm{NH_4}$, $\mathrm{h^{-1}}$, trace $V\mathrm{NO_3}$, $\mathrm{h^{-1}}$ and $\mathrm{NH_4}$, $\mu\mathrm{mol\,L^{-1}}$, (b) trace $\rho\mathrm{NH_4}$, $\mu\mathrm{mol\,L^{-1}\,h^{-1}}$, trace $\rho\mathrm{NO_3}$, $\mu\mathrm{mol\,L^{-1}\,h^{-1}}$ and chlorophyll concentration, $\mu\mathrm{g\,L^{-1}}$ for San Pablo Bay in spring, 2001. $\mathrm{NO_3}$ concentration at start was 33.6 $\mu\mathrm{mol\,L^{-1}}$.

on a daily basis and without the light limitation that results from turbulent mixing in situ. Changes in uptake of $\mathrm{NH_4}$ and $\mathrm{NO_3}$ in response to different ambient $\mathrm{NH_4}$ concentrations were measured in water from Central Bay held in experimental enclosures. Enclosure experiments (Fig. 7a–e) that contained different ambient concentrations of $\mathrm{NH_4}$ (low ambient $\mathrm{NH_4}$ <5 $\mu\mathrm{mol\,L^{-1}}$ and higher, >5 $\mu\mathrm{mol\,L^{-1}}$) showed depletion of $\mathrm{NO_3}$ to occur once $\mathrm{NH_4}$ had been reduced to low levels (Fig. 7a,b). Depletion of $\mathrm{NO_3}$ began after 1 day in the enclosures with low initial $\mathrm{NH_4}$ (enclosures A, B; Fig. 7a). In the enclosures (C, D, E, F) with higher initial ambient levels of $\mathrm{NH_4}$, there was a lag before $\mathrm{NO_3}$ was drawn down and $\mathrm{NO_3}$ concentrations in the enclosures decreased (Fig. 7b). Maximum $V\mathrm{NO_3}$ was delayed (Fig. 7c) in most of the enclosures with higher initial $\mathrm{NH_4}$ (enclosures C, E, F). Maximum specific $\mathrm{NO_3}$ uptake was reached after 2–3 days (Fig. 7c) depending on the initial concentration of $\mathrm{NH_4}$, with values of $V\mathrm{NO_3}$ exceeding those of $V\mathrm{NH_4}$. There was no change in $V\mathrm{NH_4}$ uptake with time in the enclosures (Fig. 7d). Chlorophyll *a* biomass accumulated in all enclosures reaching almost 30 $\mu\mathrm{g\,L^{-1}}$ (Fig. 7e) supported primarily by $\mathrm{NO_3}$ (Fig. 7a,b) as calculated by simple mass balance assuming 1 µg chlorophyll *a* generated for 1 µmol N taken up.

The effect of adding more $\mathrm{NH_4}$ to enclosures to see if $\mathrm{NO_3}$ uptake was suppressed was investigated in spring 2003 using 20-L enclosures filled with Central Bay water and different experimental additions of $\mathrm{NH_4}$ (5 to 30 $\mu\mathrm{mol\,L^{-1}}$). Increased $\mathrm{NH_4}$ concentration resulted in a delay of the onset of $\mathrm{NO_3}$ uptake, or increased lag time before $\mathrm{NO_3}$ depletion was observed

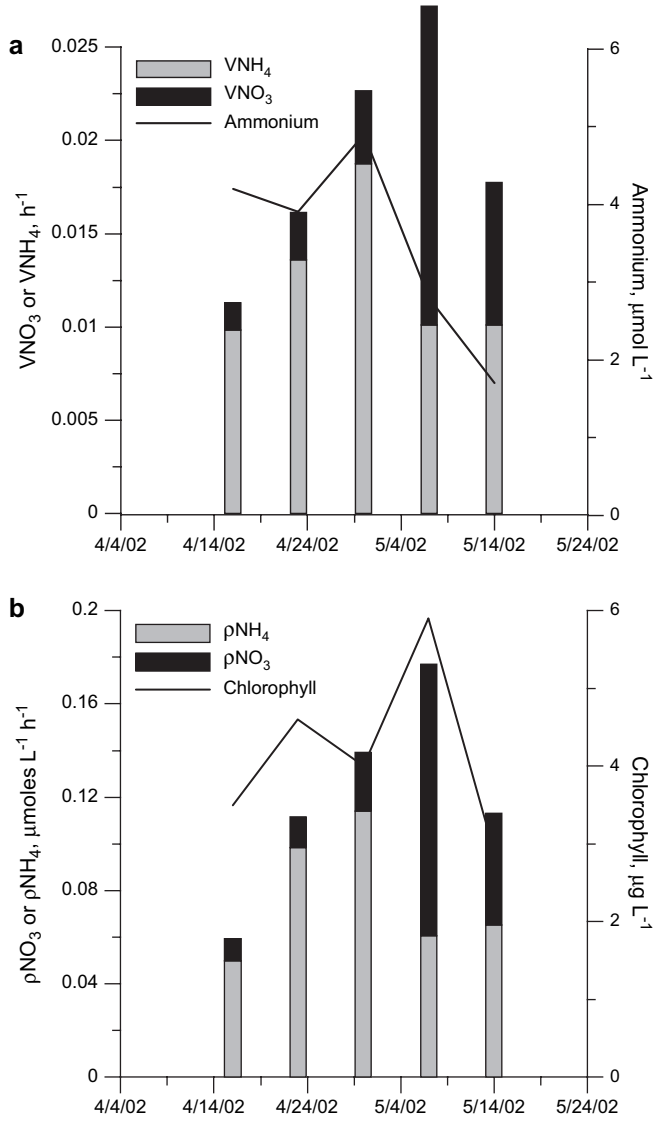


Fig. 6. (a) Trace $V\mathrm{NH_4}$, $\mathrm{h^{-1}}$, trace $V\mathrm{NO_3}$, $\mathrm{h^{-1}}$ and $\mathrm{NH_4}$, $\mu\mathrm{mol\,L^{-1}}$, (b) trace $\rho\mathrm{NH_4}$, $\mu\mathrm{mol\,L^{-1}\,h^{-1}}$, trace $\rho\mathrm{NO_3}$, $\mu\mathrm{mol\,L^{-1}\,h^{-1}}$ and chlorophyll concentration, $\mu\mathrm{g\,L^{-1}}$ for Central Bay in spring, 2002. $\mathrm{NO_3}$ concentration at start was $14\ \mu\mathrm{mol\,L^{-1}}$.

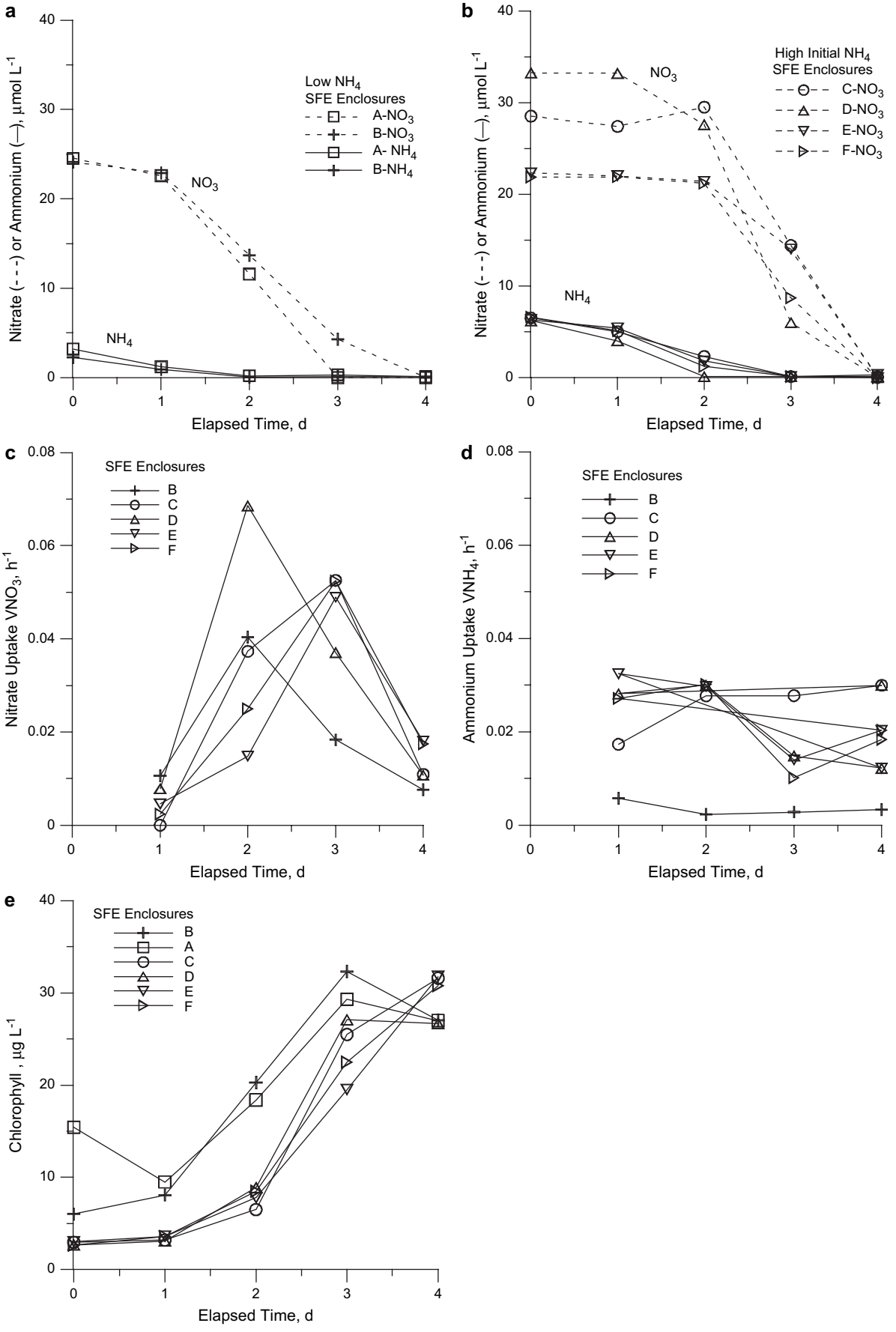
(Fig. 8a). The enclosure with no experimental addition had an initial $\mathrm{NH_4}$ concentration of $5.7\ \mu\mathrm{mol\,L^{-1}}$ and required 2 days to reduce the $\mathrm{NH_4}$ concentration to a low value ($0.8\ \mu\mathrm{mol\,L^{-1}}$; Fig. 8b), at which point $\mathrm{NO_3}$ decreased in the enclosure (Fig. 8a). At the highest addition, $30\ \mu\mathrm{mol\,L^{-1}}$, no $\mathrm{NO_3}$ decrease was observed during the 4 days of the experiment. When the values of $V\mathrm{NO_3}$ from the different sets of additions were combined for all 4 days of the experiment and plotted versus the $\mathrm{NH_4}$ concentration at the sampling time of the uptake measurement (Fig. 8c), high values of $V\mathrm{NO_3}$ appear only at low $\mathrm{NH_4}$ concentrations, ca. $1\ \mu\mathrm{mol\,L^{-1}}$. At higher $\mathrm{NH_4}$ concentrations $V\mathrm{NO_3}$ values are low, near zero rates. The pattern and values are consistent with the field data observed in the three bays (Figs. 2a and 3). The high ratio of $V\mathrm{NO_3}$ to $V\mathrm{NH_4}$ (Fig. 8d), at low $\mathrm{NH_4}$ concentrations shows the same pattern as seen for the uptake ratio in the three bays (Fig. 2b). These results demonstrate that the $\mathrm{NH_4}$ inhibition effects apparent in the bay can be experimentally reproduced by the addition of $\mathrm{NH_4}$ to SFB water, i.e. a direct demonstration of $\mathrm{NH_4}$ inhibition of $\mathrm{NO_3}$ uptake in bay water.

4. Discussion

4.1. Overview

The conditions in SFB are what have been termed for estuaries as HNLC, high nutrient low chlorophyll (Cloern, 2001) or HNLG, high nutrient low growth (Sharp, 2001). Most of the year primary production is low, and nutrients are in excess of requirements and exported from the estuary. Control of primary production in SFB was summarized by Jassby et al. (1996) as a light-limited system with nutrients assumed to be replete and non-limiting. Our results show that in addition to irradiance conditions, the details of different DIN processes need to be considered since the high $\mathrm{NO_3}$ concentrations in the estuary are generally unavailable to the phytoplankton due to the presence of $\mathrm{NH_4}$.

A modified conceptual model for the spring bloom primary production in northern San Francisco Bay based on that of Cole and Cloern (1984) and Jassby et al. (1996) and incorporating our DIN uptake results can be described by the following series of events. During winter with low irradiance conditions, primary nutrients including $\mathrm{NH_4}$ accumulate due to continuing inputs and low phytoplankton nutrient uptake activity. In spring, increases in seasonal irradiance create favorable conditions for phytoplankton growth and $\mathrm{NH_4}$ concentrations decrease due to dilution by spring runoff (Peterson et al., 1985) and by phytoplankton uptake (Fig. 4a). With sufficient time in favorable light conditions and water column stability, an initial increase in chlorophyll occurs based on $\mathrm{NH_4}$ uptake (Fig. 5b). If the combination of these processes results in $\mathrm{NH_4}$ concentrations being reduced to below $4\ \mu\mathrm{mol\,L^{-1}}$ to a value of about $1\ \mu\mathrm{mol\,L^{-1}}$ (Fig. 3), $\mathrm{NO_3}$ uptake is turned on and more chlorophyll can accumulate if irradiance conditions are still favorable. A spring bloom occurs based upon the input of both $\mathrm{NH_4}$ and the higher ambient concentration of $\mathrm{NO_3}$. Mass balance considerations indicate that to obtain the concentrations of chlorophyll measured in SFB, ambient $\mathrm{NH_4}$ is insufficient and $\mathrm{NO_3}$ must be used also. If $\mathrm{NO_3}$ uptake is not turned on, the biomass increase is small and limited to the amount of $\mathrm{NH_4}$ taken up. In years with insufficient dilution, and higher levels of $\mathrm{NH_4}$ (i.e. $>4\ \mu\mathrm{mol\,L^{-1}}$) no spring blooms occur (e.g. Suisun Bay in 2001, 2002). The spring bloom, if it occurs, is terminated by nutrient depletion, unfavorable light/stability conditions, or grazing and the phytoplankton population crashes. As the bloom fades, the combination of low rates of phytoplankton uptake of $\mathrm{NH_4}$ and regeneration of the bloom-produced organic nitrogen by grazing or by bacterial action at the sediment surface (Caffrey, 1995) results in $\mathrm{NH_4}$ concentrations returning to levels inhibiting $\mathrm{NO_3}$ uptake. Similar observations have been described for Delaware Bay (Sharp et al., 1984; Pennock and Sharp, 1994; Yoshiyama and Sharp, 2006) with


a
Low NH4
SFE Enclosures
A-NO3
B-NO3
A- NH4
B-NH4
NO3
NH4
Nitrate (- - -) or Ammonium (—), µmol L-1
Elapsed Time, d
b
High Initial NH4
SFE Enclosures
C-NO3
D-NO3
E-NO3
F-NO3
NO3
NH4
Nitrate (- - -) or Ammonium (—), µmol L-1
Elapsed Time, d
c
SFE Enclosures
B
C
D
E
F
Nitrate Uptake VNO3, h-1
Elapsed Time, d
d
SFE Enclosures
B
C
D
E
F
Ammonium Uptake VNH4, h-1
Elapsed Time, d
e
SFE Enclosures
B
A
C
D
E
F
Chlorophyll , µg L-1
Elapsed Time, d

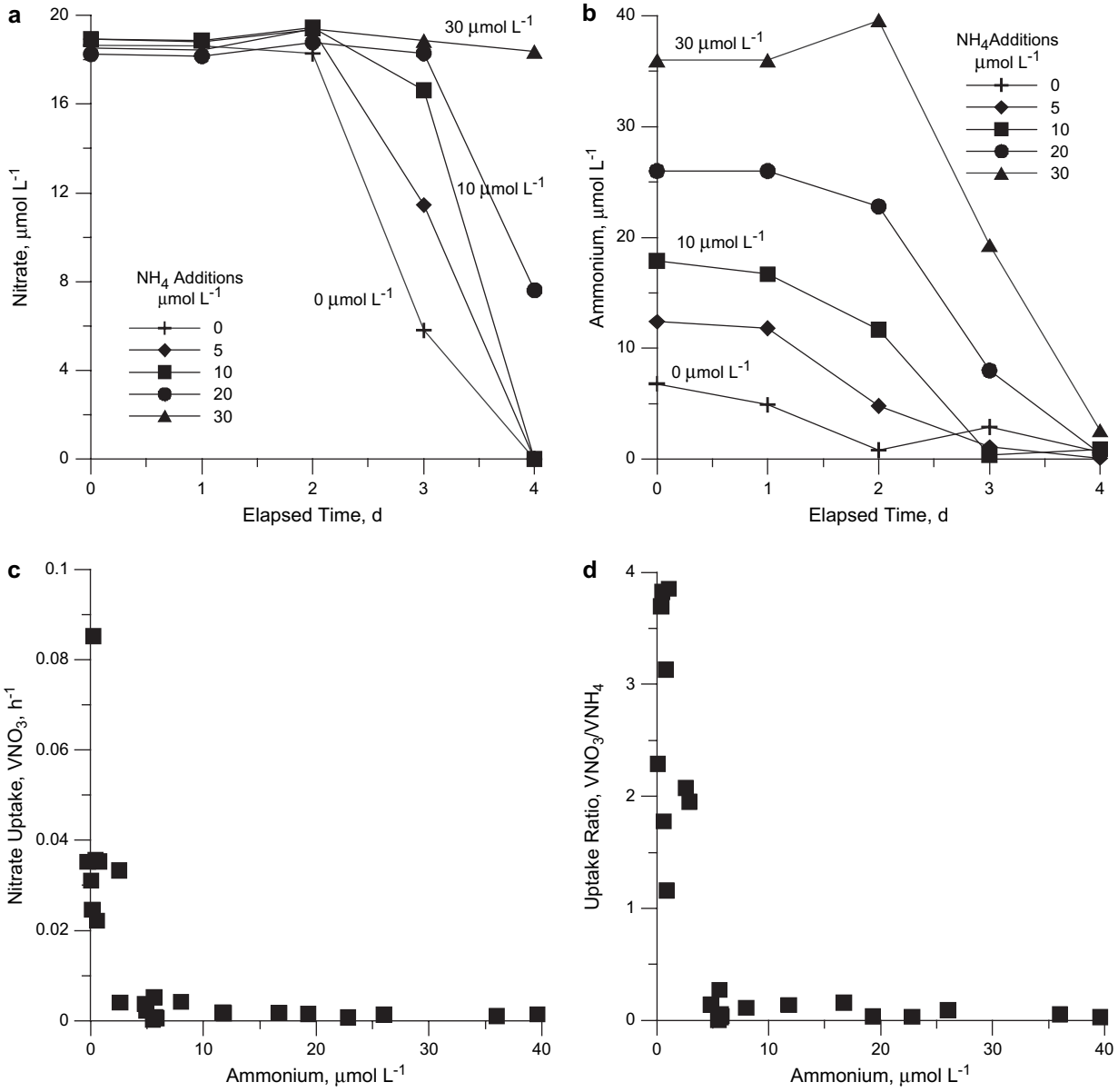


Fig. 8. Results from enclosures filled with Central Bay water in spring 2003 treated with NH_4 additions of 0, 5, 10, 20, 30 µmol L^{-1} and followed for 4 days. (a) NO_3, µmol L^{-1}, (b) NH_4, µmol L^{-1} plotted against elapsed time, (c) trace VNO_3, h^{-1}, (d) ratio of trace VNO_3:VNH_4 plotted against the NH_4, µmol L^{-1} at the sampling time of the uptake measurement.

spring blooms initiated by NH_4, and after exhaustion of NH_4 significant uptake of NO_3, that is followed by a return in summer to the use of NH_4.

4.2. Predicting the time scale for bloom development

Based on these results, within the time frame of a favorable irradiance/stability event (e.g. neap tides, low wind, high incoming irradiance), a critical process for bloom development in SFB is the reduction of NH_4 concentration to values allowing NO_3 uptake to take place. The time required to reduce NH_4 concentrations, from the typical high levels in SFB, to reduced inhibitory levels for NO_3 uptake (i.e. to about 50% inhibition at 1 µmol L^{-1} NH_4) can be calculated for different bays in different seasons, assuming sufficient time with favorable irradiance, as:

$$\text{Time to 1 } \mu\text{mol L}^{-1}\ \text{NH}_4 = (\text{NH}_{4(\text{initial})} - 1)/\rho\text{NH}_4 \quad (1)$$

where ρNH_4 is the measured mean ρNH_4 value. Values calculated from Eq. (1) using the seasonal mean NH_4 concentrations and NH_4 uptake rates (from Wilkerson et al., 2006) are

Fig. 7. Results from enclosures filled with Central Bay water in spring 1999 that contained low (enclosures A, B) or high ambient initial NH_4 (enclosures C, D, E, F); all frames show results against elapsed time up to 4 days. (a) NO_3 and NH_4 concentration, µmol L^{-1} in enclosures A and B (low NH_4), (b) NO_3 and NH_4 concentrations, µmol L^{-1} in enclosures C–F (high NH_4), (c) trace VNO_3, h^{-1}, (d) trace VNH_4, h^{-1} versus elapsed time in enclosures B through F. No ^{15}N data are available for enclosure A. (e) Chlorophyll concentration (µg L^{-1}) in enclosures A–F.

presented in Table 1. On the assumption that a day on each side of neap tide for a total of 3 days would provide sufficiently improved irradiance conditions to allow NH_4 uptake to increase and to occur at the mean rates shown in Table 1, the potential for bloom development in the three bays can be assessed (Table 1). In this scenario, spring blooms could be initiated by a 3-day irradiance/stability event in both San Pablo and Central Bays since the depletion times (to reach 1 μmol L^{-1}) are just below 3 days for each bay. In summer, the unfavorable times for depletion of NH_4 in San Pablo and Central Bays, 8.5 and 8.4 days, respectively, are due largely to the almost 2-fold decrease in mean NH_4 uptake in summer. Unfavorable conditions in Suisun Bay for both seasons, 15 days in spring and 9.6 days in summer for NH_4 to reach 1 μmol L^{-1}, are due to both low NH_4 uptake rates, which do not increase in spring as occurs in the other two bays, (a condition also measured in recent enclosure experiments, A. Parker, pers. comm.) and to high mean NH_4 concentrations. The reason for this low NH_4 uptake condition is unknown at present. This analysis is consistent with the lack of observed blooms in summer in all three bays and the observation of spring blooms only in San Pablo and Central Bays (excepting the 2000 bloom in Suisun when there were low ambient NH_4 concentrations, Wilkerson et al., 2006).

This analysis of the conditions for bloom initiation in San Francisco Bay is a worst-case scenario, and conservative since it uses mean values for NH_4 uptake. It is likely that after 1 or 2 days of good irradiance/stability conditions, the NH_4 uptake rate would increase above the mean value and shorten the time to reach 1 μmol L^{-1} NH_4, when high rates of NO_3 uptake would occur. In enclosure experiments, NH_4 uptake rates increased with time and resulted in rapid reduction in NH_4 to zero in 2–3 days in the enclosure experiments. Besides time to reduce ambient NH_4 to non-inhibitory levels, bloom formation also requires more time with sufficient light for NO_3 uptake and assimilation and for biomass to be synthesized. Enclosure experiments indicate this time to be a further 2–3 days, i.e. with sufficient irradiance and water stability, and a low ambient NH_4, a bloom could develop in 5–6 days. This scenario (based upon data from northern SFB) is consistent with the time scales of the model and field data for South SFB reported by Cloern (1991), who analyzed the effects of the spring and neap tide cycles on the development of phytoplankton blooms and showed chlorophyll concentrations increased from 4 to as high as 32 μg L^{-1} by day 6 of a neap tide cycle.

4.3. Consequences of high NH_4 loading

NH_4 inhibition of NO_3 uptake contributes to a reduction in primary production in SFB by shutting off phytoplankton access to the larger reservoir of inorganic nitrogen, e.g. the mean concentration of NH_4 in San Pablo Bay in winter is 8 μmol L^{-1} and that of NO_3 is 26.9 μmol L^{-1} (Wilkerson et al., 2006). If chlorophyll were to be produced in a spring bloom equally by consuming either NH_4 at 8 μmol L^{-1} or NO_3 at 26.8 μmol L^{-1}, an NO_3-based bloom would produce ca. 3.4 times as much chlorophyll as one based on NH_4 alone; or if both sources were fully utilized, the resulting chlorophyll would be 4.4 times that of an NH_4-only bloom.

The potential effect of NH_4 inhibition of NO_3 uptake modulating primary production in other estuaries will depend upon the nature of any other nutrient limitation, e.g. there may be no effect on a phosphate (PO_4) or silicate ($Si(OH)_4$) limited system. However, if substantial NH_4 is present (>4 μmol L^{-1}) then NO_3 should be eliminated as an accessible DIN source in any nutrient ratio calculation. Using mean concentrations in Central Bay of SFB in summer (from Table 1 and Wilkerson et al., 2006), $Si(OH)_4 = 73.0$ μmol L^{-1}, $NO_3 = 20.7$ μmol L^{-1}, $NH_4 = 4.9$ μmol L^{-1}, $PO_4 = 2.9$ μmol L^{-1}, Central Bay is clearly N limited (with a ratio of P to available DIN of 1:1.7), despite the presence of considerable NO_3. The Central Bay primary production ecosystem is likely regulating in summer on NH_4 through a combination of inputs from anthropogenic sources, by regeneration at the sediment surface and by grazing. The quasi-steady state concentration of NH_4 makes the NO_3 pool invisible to the ecosystem.

Irradiance and physical conditions are important in determining the outcome of NH_4 inhibition on productivity. In other estuaries with irradiance conditions that are favorable for long periods of time (unlike SFB) accompanied by high NH_4 inputs, blooms of the type described for SFB will occur more regularly as a result of sufficient light and drawdown of NH_4 to non-inhibiting concentrations. For example, the decade-long time series of weekly nutrients and chlorophyll in the Skidaway River estuary (Verity, 2002a,b) shows one or two strong seasonal blooms each year with chlorophyll concentrations up to 20 μg L^{-1}. NH_4 concentrations can be as high as 10 μmol L^{-1} but appear to be drawn down to a range 0.1 to 1 μmol L^{-1} that allows access to NO_3 which is drawn down from 10 to 0 μmol L^{-1}, with accompanying increase in chlorophyll of up to 20 μg L^{-1}; values that would require the sum of NO_3 and NH_4 uptake to occur.

Table 1
Days to deplete ambient NH_4 to 1 μmol L^{-1} calculated for Central, San Pablo and Suisun Bays using mean values for spring (March, April, and May) and summer (June, July, and August)

Bay	Spring			Summer		
	Days to 1 μmol L^{-1}	Mean NH_4 (μmol L^{-1})	Mean ρNH_4 (nmol L^{-1} h^{-1})	Days to 1 μmol L^{-1}	Mean NH_4 (μmol L^{-1})	Mean ρNH_4 (nmol L^{-1} h^{-1})
Central	2.7	3.2	67.76	8.4	4.9	38.46
San Pablo	2.8	3.5	75.63	8.5	4.1	30.50
Suisun	15	6.8	32.23	9.6	5.3	37.30

4.4. Implications for management

Many rivers and estuaries of the U.S. are experiencing increasing loads of NH_4 (Paerl, 1999). An understanding of the critical role of anthropogenic NH_4 input could provide a powerful tool for management of estuarine productivity, since typically the proportion of the anthropogenic input/loading of NH_4 in these regions can be controlled by changes in water treatment practices and water allocation (dilution). Some agricultural practices could be modified to reduce NH_4 inputs as well. Regulating NH_4 emissions/dilution may be a useful tool in managing food web structure and healthy primary production (Nixon and Buckley, 2002) in eutrophic regions that do not have excessive phytoplankton buildup or reduced oxygen concentrations. For example, the conversion of NH_4 to NO_3 by advanced secondary treatment would make all forms of DIN available for primary production with substantial increases in potential phytoplankton biomass and primary production in spring, and perhaps in summer as well, in SFB.

Climate change will modulate the impact of NH_4 on bloom formation. The basic pattern of NH_4 distribution in SFB in winter is the result of mixing between water with high NH_4 and low salinity at the head of the estuary, and low NH_4 and high salinity at the seaward end (Peterson et al., 1985; Wilkerson et al., 2006). However, river runoff to the SFB is highly variable (Schemel and Hager, 1986) and the NH_4 concentration in the northern part of the bay may be reduced to near zero in wet years (Peterson et al., 1985) by dilution. In dry years, the concentration of NH_4 remains high or is increased and up to 80% of the NH_4 in northern SFB may be due to sewage treatment effluent and agricultural drainage (Hager and Schemel, 1992). Dry years have already been associated with low chlorophyll (Lehman, 1996) with negative consequences for higher trophic levels that are adapted to the spring bloom productivity period.

4.5. Implications for decline in productivity observed in SFB

During the period 1975–1995, the upper reaches of the SFB experienced a long term decline in primary production, chlorophyll concentration (Jassby et al., 2002), zooplankton abundance (Kimmerer, 2002) and fish populations (Bennett and Moyle, 1996). Water transparency (which increased) was eliminated as a cause of the decline in productivity, as were changes in river flow (Jassby et al., 2002). Increased grazing, resulting from the invasion of Suisun Bay by the exotic clam *Corbula amurensis* in 1987–1999 (Nichols et al., 1990), was thought to contribute to the same. However, the decline in chlorophyll began prior to the appearance of *C. amurensis* in 1987, declining from 13 $\mu g\,L^{-1}$ to 7 $\mu g\,L^{-1}$ from 1978 to 1986 (Fig. 5 in Alpine and Cloern, 1992) suggesting some other causal factor, possibly increased NH_4 inputs (due to changes in sewage treatment practices), in place prior to the appearance of the clams. After 1987, the biomass of chlorophyll in Suisun Bay in summer has remained low, coinciding with the arrival of the invasive clam, *C. amurensis*, population which has the capability of filtering the entire water column in less than 1 day (Thompson, 2000).

Suisun Bay annual productivity is negatively influenced in different ways in spring and in summer. Strong spring blooms can occur as in 2000, but are usually suppressed by high NH_4. The invasive clam *Corbula* is not abundant in spring. However, in summer Suisun Bay productivity is held to low levels by clam grazing. Clam grazing ensures the inability of the phytoplankton to build phytoplankton biomass and access NO_3 in two ways, by holding chlorophyll levels too low to reduce NH_4 to non-inhibitory levels, and by regenerating a portion of the assimilated nitrogen and contributing to the ambient NH_4 pool. The effect of the clams in Suisun Bay impacts the seaward bays (San Pablo and Central Bays) as well with more NH_4 exported southward than would be the case if the Suisun phytoplankton were able to process riverine NH_4 more effectively. In effect, the net retention of NH_4 in Suisun Bay is currently low, since phytoplankton are growing solely on NH_4 at a low rate, and the clams are regenerating a portion of productivity as NH_4 to be advected seaward. The large summer chlorophyll concentrations characteristic of Suisun Bay in the late 1970s may have been the result of efficient processing of advected riverine nutrients as NH_4 inputs may have been lower at that time, opening the window for NO_3 uptake by phytoplankton and by the buildup of chlorophyll biomass in the absence of such strong grazing.

Nutrient concentrations into the Delta and SFB have increased over the last 50 years from increased use of fertilizers, runoff from dairies and treatment plant effluents (Kratzer and Shelton, 1998) and should have increased primary productivity. More specifically one form of DIN, NH_4 probably increased in the early 1980s, when waste water dischargers were required to add basic secondary treatment, converting organic nitrogen to NH_4 (L. Kolb, pers. comm.). This attempt to improve water quality in the estuary may have contributed to a long term decline in SFB productivity at all levels, resulting from NH_4 inhibition of NO_3 uptake and chlorophyll accumulation. We suspect other U.S. estuarine ecosystems, may be impacted by increased inputs of NH_4. There may also be complications due to the increased input of another anthropogenic source of N, urea from increased use of urea-based agricultural fertilizers (Glibert et al., 2006). Examination of some of these ecosystems for changes in NH_4, as has been carried out for urea, beginning with the federally mandated switch to secondary sewage treatment in the 1980s might prove interesting and useful for development of management tools.

5. Conclusions

Low annual primary production in SFB is due primarily to turbid conditions but is also modulated by high NH_4 inputs and concentrations that can suppress access to NO_3 by phytoplankton and may reduce the occurrence of spring blooms and quantity of accumulated chlorophyll. Since the NH_4 concentrations at the end of winter are diluted by precipitation and runoff, and because the seasonal precipitation and runoff are

highly variable, the spring primary productivity is even more variable than if it were only a function of turbidity and water column stability. Secondary production processes by higher trophic levels dependent on the timing and quantity of spring bloom phytoplankton will be adversely affected by the disturbances brought about by increased anthropogenic inputs of NH_4. These results offer a basis both for understanding recent historical changes in similar turbid estuaries modulated by anthropogenic inputs of inorganic nitrogen and for the establishment of potential strategies for managing the timing and magnitude of estuarine primary production.

Acknowledgments

This research was supported by the USA Environmental Protection Agency (EPA) Science to Achieve Results (STAR) program award #827644-01-0 and the University of Southern California SeaGrant Program. We wish to thank the crew of the R/V Questuary for their help with the sampling program (Captain David Morgan and Jay Tustin). Special thanks to James Cloern, Jonathan Sharp, Alex Parker and Wim Kimmerer for helpful discussions.

References

Alpine, A.E., Cloern, J.E., 1992. Trophic interactions and direct physical effects control phytoplankton biomass and production in an estuary. Limnology and Oceanography 37, 946–955.

Arar, E.J., Collins, G.B., 1992. In vitro determination of chlorophyll *a* and phaeophytin *a* in marine and freshwater phytoplankton by fluorescence – USEPA Method 445.0. USEPA Methods for Determination of Chemical Substances in Marine and Estuarine Environmental Samples. Cincinnati.

Bennett, W.A., Moyle, P.B., 1996. Where have all the fishes gone? Interactive factors producing fish declines in the Sacramento-San Joaquin Estuary. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. AAAS, San Francisco, pp. 519–544.

Caffrey, J.M., 1995. Spatial and seasonal patterns in sediment nitrogen remineralization and ammonium concentrations in San Francisco Bay, California. Estuaries 18, 219–233.

Cloern, J.E., 1987. Turbidity as a control on phytoplankton biomass and productivity in estuaries. Continental Shelf Research 7, 1367–1381.

Cloern, J.E., 1991. Tidal stirring and phytoplankton bloom dynamics in an estuary. Journal of Marine Research 49, 203–221.

Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology Progress Series 210, 223–253.

Cloern, J.E., Dufford, R., 2005. Phytoplankton community ecology: principles applied in San Francisco Bay. Marine Ecology Progress Series 285, 11–28.

Cochlan, W.P., Harrison, P.J., 1991. Inhibition of nitrate uptake by ammonium and urea in the eukaryotic picoflagellate *Micromonas pusilla* (Butcher) Manton et Parke. Journal of Experimental Marine Biology and Ecology 153, 143–152.

Codispoti, L.A., 1985. Nitrogen in upwelling systems. In: Carpenter, E.J., Capone, D.G. (Eds.), Nitrogen in the Marine Environment. Academic Press, New York, pp. 513–565.

Codispoti, L.A., Dugdale, R.C., Minas, H.J., 1982. A comparison of the nutrient regimes off northwest Africa, Peru and Baja California. Rapports et Proces verbeaux Réunion Conseil Internationale. Exploration du Mer 180, 184–201.

Cole, B.E., Cloern, J.E., 1984. Significance of biomass and light availability to phytoplankton productivity in San Francisco Bay. Marine Ecology Progress Series 17, 15–24.

Conway, H.L., 1977. Interactions of inorganic nitrogen in the uptake and assimilation by marine phytoplankton. Marine Biology 39, 221–232.

Dortch, Q., 1990. The interaction between ammonium and nitrate uptake in phytoplankton. Marine Ecology Progress Series 61, 138–201.

Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. Limnology and Oceanography 12, 196–206.

Dugdale, R.C., Hopkins, T.S., 1978. Predicting the structure and dynamics of a pollution-driven marine ecosystem embedded in an oligotrophic sea. Thalassia Jugoslavica 14, 107–126.

Dugdale, R.C., MacIsaac, J.J., 1971. A computational model for the uptake of nitrate in the Peru upwelling region. Investigacion Pesquera 35, 299–308.

Dugdale, R.C., Wilkerson, F.P., 1986. The use of ^{15}N to measure nitrogen uptake in eutrophic oceans; experimental considerations. Limnology and Oceanography 31, 673–689.

Dugdale, R.C., Wilkerson, F.P., Marchi, A., Hogue, V., 2006. Nutrient controls on new production in the Bodega Bay, California, coastal upwelling plume. Deep-Sea Research II 53, 3049–3062.

Glibert, P.M., Harrison, J., Heil, C., Seitzinger, S., 2006. Escalating worldwide use of urea – a global change contributing to coastal eutrophication. Biogeochemistry 77, 441–463.

Hager, S.W., Schemel, L.E., 1992. Sources of nitrogen and phosphorus to northern San Francisco Bay. Estuaries 15, 40–52.

Hogue, V.E., 2000. Ultraviolet radiation effects on natural phytoplankton assemblages of central San Francisco Bay. M.A. Thesis, San Francisco, San Francisco State University.

Hogue, V.E., Wilkerson, F.P., Dugdale, R.C., 2005. Ultraviolet-B radiation effects on natural phytoplankton assemblages of central San Francisco Bay. Estuaries 29, 190–203.

Jassby, A.D., Koseff, J.R., Monismith, S.G., 1996. Processes underlying phytoplankton variability in San Francisco Bay. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. AAAS, San Francisco, pp. 325–349.

Jassby, A.D., Cloern, J.E., Cole, B.E., 2002. Annual primary production: patterns and mechanisms of change in a nutrient-rich tidal ecosystem. Limnology and Oceanography 47, 698–712.

Kimmerer, W.J., 2002. Effects of freshwater flow on abundance of estuarine organisms: physical effects or trophic linkages? Marine Ecology Progress Series 243, 39–55.

Kratzer, C.R., Shelton, J.L., 1998. Water quality assessment of the San Joaquin–Tulare Basins, California. Analysis of available data on nutrients and suspended sediment in surface water, 1972–1990, USGS Professional Paper 1587.

Lehman, P., 1996. Changes in chlorophyll *a* concentration and phytoplankton community composition with water-year type in the upper San Francisco Bay Estuary. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. AAAS, San Francisco, pp. 351–374.

Nichols, F.H., Thompson, J., Schemel, L.E., 1990. Remarkable invasion of San Francisco Bay (California, USA) by the Asian clam *Potamocorbula amurensis*. II. Displacement of a former community. Marine Ecology Progress Series 66, 95–101.

Nixon, S.W., Buckley, B.A., 2002. A strikingly rich zone-nutrient enrichment and secondary production in coastal marine ecosystems. Estuaries 25, 782–796.

Paerl, H.W., 1999. Cultural eutrophication of shallow coastal waters: coupling changing anthropogenic nutrient inputs to regional management approaches. Limnologica 29, 249–254.

Pennock, J.R., 1987. Temporal and spatial variability in phytoplankton ammonium and nitrate uptake in the Delaware Bay. Estuarine, Coastal and Shelf Science 24, 841–857.

Pennock, J.R., Sharp, J.H., 1994. Temporal alternation between light- and nutrient-limitation of phytoplankton production in a coastal plain estuary. Marine Ecology Progress Series 111, 275–288.

Peterson, D.H., Smith, R.E., Hager, S.W., Harmon, D.D., Herndon, R.E., Schemel, L.E., 1985. Interannual variability in dissolved inorganic nutrients in northern San Francisco Bay estuary. Hydrobiologia 129, 37–58.

Schemel, L.E., Hager, S.W., 1986. Chemical variability in the Sacramento River and in northern San Francisco Bay. Estuaries 9, 270–283.

Sharp, J.H., 2001. Marine and aquatic communities, stress from eutrophication. In: Encyclopedia of Biodiversity, vol. 4. Academic Press, pp. 1–11.

Sharp, J.H., Pennock, J.R., Church, T.M., Tramontano, J.M., Cifuentes, L.A., 1984. The estuarine interactions of nutrients, organics and metals: a case study in the Delaware Estuary. In: Kennedy, V.S. (Ed.), The Estuary as a Filter. Academic Press, Orlando, FL, pp. 241–258.

Solorzano, L., 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnology and Oceanography 14, 799–810.

Syrett, P.J., 1981. Nitrogen metabolism of microalgae. In: Platt, T. (Ed.), Canadian Bulletin of Fisheries and Agriculture Sciences 210, pp. 234–250.

Thompson, J.K., 2000. Two stories of phytoplankton control by bivalves in San Francisco Bay: the importance of spatial and temporal distribution of bivalves. Journal of Shellfish Research 19, 612.

Verity, P.G., 2002a. A decade of change in the Skidaway River estuary. I. Hydrography and nutrients. Estuaries 25, 944–960.

Verity, P.G., 2002b. A decade of change in the Skidaway River estuary. II. Particulate organic carbon, nitrogen, and chlorophyll *a*. Estuaries 25, 961–975.

Whitledge, T.E., Malloy, S.C., Patton, C.J., Wirick, C.D., 1981. Automated Nutrient Analysis in Seawater, Report BNL 51398. Brookhaven National Laboratory, Upton, NY, 216 pp.

Wilkerson, F.P., Dugdale, R.C., 1992. Measurements of nitrogen productivity in the Equatorial Pacific. Journal of Geophysical Research 97, 669–679.

Wilkerson, F.P., Dugdale, R.C., Hogue, V.E., Marchi, A., 2006. Phytoplankton blooms and nitrogen productivity in San Francisco Bay. Estuaries and Coasts 29, 401–416.

Yoshiyama, K., Sharp, J.H., 2006. Phytoplankton response to nutrient enrichment in an urbanized estuary: apparent inhibition of primary production by over-eutrophication. Limnology and Oceanography 51, 424–434.