

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

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Received 19 April 2006; accepted 13 December 2006

Available online 2 February 2007

## Abstract

The substantial inventory of nitrate ( $\text{NO}_3$ ) in San Francisco Bay (SFB) is unavailable to the resident phytoplankton most of the year due to the presence of ammonium ( $\text{NH}_4$ ) at inhibitory concentrations that prevents  $\text{NO}_3$  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  $\text{NH}_4$  concentrations are low,  $<4 \mu\text{mol L}^{-1}$  and  $\text{NO}_3$  uptake by phytoplankton occurs. Field measurements and enclosure experiments confirm the  $\text{NH}_4$  inhibition process to be the cause of low  $\text{NO}_3$  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,  $\text{NH}_4$  concentrations must be reduced to a critical range, 1 to  $4 \mu\text{mol L}^{-1}$  through dilution by precipitation and by phytoplankton uptake. This enables rapid uptake of  $\text{NO}_3$  and subsequent increase in chlorophyll. The resulting bloom is due to both the initial uptake of  $\text{NH}_4$  and the subsequent uptake of  $\text{NO}_3$ . The  $\text{NO}_3$  uptake step is crucial since it is the larger nitrogen source and uptake occurs at higher rates than that for  $\text{NH}_4$  at the concentrations that occur in SFB. Existing models of light-limited, non-nutrient limited productivity in SFB require modification to include the  $\text{NH}_4$  inhibition effect. From measured  $\text{NH}_4$  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  $\text{NH}_4$  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  $\text{NH}_4$  concentration prior to the productivity season.  $\text{NH}_4$  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.

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*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

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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  $\text{NH}_4$  and  $\text{NO}_3$  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  $\text{NH}_4$  as a nitrogen source since the energetic costs of assimilating that species of nitrogen are less than that for  $\text{NO}_3$ . By inference, an estuary whose phytoplankton are utilizing  $\text{NH}_4$  for growth should have the same primary productivity as if they were using  $\text{NO}_3$ , or perhaps even higher productivity on  $\text{NH}_4$  compared to  $\text{NO}_3$ .

The ability to separate out the use of  $\text{NO}_3$  and  $\text{NH}_4$  by phytoplankton in the marine environment was pioneered by Dugdale and Goering (1967) using the stable isotope  $^{15}\text{N}$  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  $\text{NO}_3$  since  $\text{NH}_4$  is readily oxidized to  $\text{NO}_3$  and is the minor inorganic species (Codispoti, 1985). Although under some culture conditions algae use both forms of DIN simultaneously (Dortch, 1990),  $\text{NO}_3$  uptake is suppressed or inhibited by relatively low concentrations of  $\text{NH}_4$  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  $^{15}\text{N}$  have confirmed the relationship between elevated  $\text{NH}_4$  concentrations and low  $\text{NO}_3$  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,  $\text{NO}_3$  uptake was negatively correlated and reduced to low levels with ambient  $\text{NH}_4$  concentrations in the range of 1–2.5  $\mu\text{mol L}^{-1}$ .  $^{15}\text{N}$  studies in a series of upwelling sites, from Baja California to northwest Africa and Peru showed maximum specific  $\text{NO}_3$  uptake rates to always exceed maximum specific  $\text{NH}_4$  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  $\text{NO}_3$  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  $\text{NO}_3$  than when growing on  $\text{NH}_4$ . However, if  $\text{NH}_4$  is at an inhibitory level, this form of DIN may not allow the high  $\text{NO}_3$ -based productivity. San Francisco Bay, as an urban estuary impacted by anthropogenic inputs and with the likelihood of high  $\text{NH}_4$  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  $^{15}\text{N}$  and found

that  $\text{NH}_4$  uptake by phytoplankton in Central SFB dominated DIN uptake and that  $\text{NO}_3$  uptake was a rare occurrence in spite of abundant ambient  $\text{NO}_3$  concentrations (Hogue et al., 2005). Similar observations were made for the Delaware Estuary (Pennock, 1987) where  $\text{NH}_4$  fuels productivity in a high  $\text{NO}_3$  setting. Most annual primary production in central SFB depended upon  $\text{NH}_4$  (Hogue et al., 2005) except during spring when ambient  $\text{NH}_4$  concentrations fell to low values and high levels of primary production based on  $\text{NO}_3$  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  $\text{NH}_4$  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  $\text{NO}_3$  uptake than  $\text{NH}_4$  uptake indicating higher growth rates on  $\text{NO}_3$  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  $\mu\text{g L}^{-1}$  chlorophyll. This occurred when there were very low salinity values and low  $\text{NH}_4$  concentrations, neither of which occurred there in 2001 or 2002 (Wilkerson et al., 2006), accompanied by high  $\text{NO}_3$  uptake rates. This suggested that  $\text{NH}_4$  played a role in bloom dynamics, by limiting phytoplankton access to the  $\text{NO}_3$  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  $\text{NO}_3$  and accumulate chlorophyll during spring blooms. We evaluate the role of two components of the DIN pool (i.e.  $\text{NH}_4$  and  $\text{NO}_3$ ) 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  $^{15}\text{N}$  labeled  $\text{NO}_3$  or  $\text{NH}_4$  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  $\text{NH}_4$  or treated with different additions of  $\text{NH}_4$ . 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  $\text{NH}_4$  concentrations. In April 2003, an enclosure experiment was conducted in which additions of  $\text{NH}_4$  (5 to 30  $\mu\text{mol L}^{-1}$  of  $\text{NH}_4\text{Cl}$ ) 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  $^{15}\text{NO}_3$  or  $^{15}\text{NH}_4$ .

## 2.3. Analytical methods

$\text{NO}_3$  concentrations were determined using a Bran and Lubbe AutoAnalyzer II (Whitledge et al., 1981) and  $\text{NH}_4$  using a spectrophotometer according to Solorzano (1969). Water samples were prefiltered using precombusted GF/F filters before  $\text{NH}_4$  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  $^{15}\text{N}$  additions to SFB water or water sampled from enclosures and the  $^{15}\text{N}$  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.  $^{15}\text{N}$  inoculations were of trace additions (approximately 10% of ambient DIN concentrations) or saturated (5  $\mu\text{mol L}^{-1}$ ) additions of either  $\text{K}^{15}\text{NO}_3$  or  $^{15}\text{NH}_4\text{Cl}$  (99 atom%  $^{15}\text{N}$ ). 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  $^{15}\text{N}$  enrichment with a Europa Tracermass (Wilkerson and Dugdale, 1992) or PDZ 20/20 mass spectrometer system. The transport rates ( $\rho$ , in  $\mu\text{mol L}^{-1} \text{h}^{-1}$ ) and *V* (biomass specific uptake in  $\text{h}^{-1}$ ) 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,  $\text{NH}_4$ , and  $\text{NO}_3$  and

uptake of  $^{15}\text{NO}_3$  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  $\text{NH}_4$  concentrations, often near zero (Fig. 1b). In Suisun Bay, only one bloom was observed, in 2000 that occurred when  $\text{NH}_4$  concentrations were low in the spring, in contrast to the other years when  $\text{NH}_4$  levels were high. The chlorophyll peaks in all bays were coincident with peaks in  $^{15}\text{NO}_3$  uptake (Fig. 1c) that was otherwise very low (almost zero) the rest of the time. In all three bays sampled, concentrations of  $\text{NH}_4$  were above 4  $\mu\text{mol L}^{-1}$  most of the year (Fig. 1b), except during the spring bloom periods. Nitrate was high (non-limiting), >20  $\mu\text{mol L}^{-1}$  most of the year (Fig. 1d). Winter uptake rates were lowest of all seasons probably due to poor irradiance conditions.

When all the  $^{15}\text{NO}_3$  uptake rates collected from the three bays are plotted versus  $\text{NH}_4$  concentration (Fig. 2a), a distinct threshold is seen such that very low  $\text{NO}_3$  uptake occurs at higher  $\text{NH}_4$  concentrations (>4  $\mu\text{mol L}^{-1}$ ). The ratio of  $\rho\text{NO}_3$  to  $\rho\text{NH}_4$  uptake shows the same trend with low ratios at high  $\text{NH}_4$  concentrations (Fig. 2b). The symbols used for these ratios are bubbles that reflect the chlorophyll concentration. With low  $\text{NH}_4$  concentrations (i.e. <4  $\mu\text{mol L}^{-1}$ ), there are higher ratios of  $\rho\text{NO}_3$  to  $\rho\text{NH}_4$  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  $\text{NO}_3$  uptake occurs and that  $\text{NO}_3$  uptake only takes place at lower ambient  $\text{NH}_4$  concentrations.

To observe this relationship during just the spring bloom periods, biomass specific nitrate uptake rates,  $\text{VNO}_3$  versus ambient  $\text{NH}_4$ , 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  $\text{VNO}_3$  at  $\text{NH}_4$  concentrations below about 4  $\mu\text{mol L}^{-1}$   $\text{NH}_4$  likely caused by  $\text{NH}_4$  inhibition of  $\text{NO}_3$  uptake. A variety of mathematical formulations of  $\text{NO}_3$  uptake inhibition by  $\text{NH}_4$  have been described including both linear and exponential (Dortch, 1990). Cochlan and Harrison (1991) fitted experimental data of  $\text{NH}_4$  inhibition of  $\text{NO}_3$  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,  $\ln \text{VNO}_3 = -1.28 \times \ln [\text{NH}_4] - 4.26$  (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  $\text{NO}_3$  uptake at elevated  $\text{NH}_4$  concentrations are consistent with interpretation as the result of  $\text{NH}_4$  inhibition.

When  $\text{NH}_4$  uptake is plotted versus  $\text{NH}_4$  for San Pablo and Central Bays using spring data (Fig. 4a), a pattern opposite to that of  $\text{VNO}_3$  results, i.e. decreasing  $\text{VNH}_4$  with decreasing  $\text{NH}_4$  concentrations, that can be fit with a straight line ( $\text{VNH}_4 = 0.025 \times [\text{NH}_4]$ ) with an  $r^2$  of 0.9. The relationship for  $\text{VNH}_4$  versus  $\text{NH}_4$  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

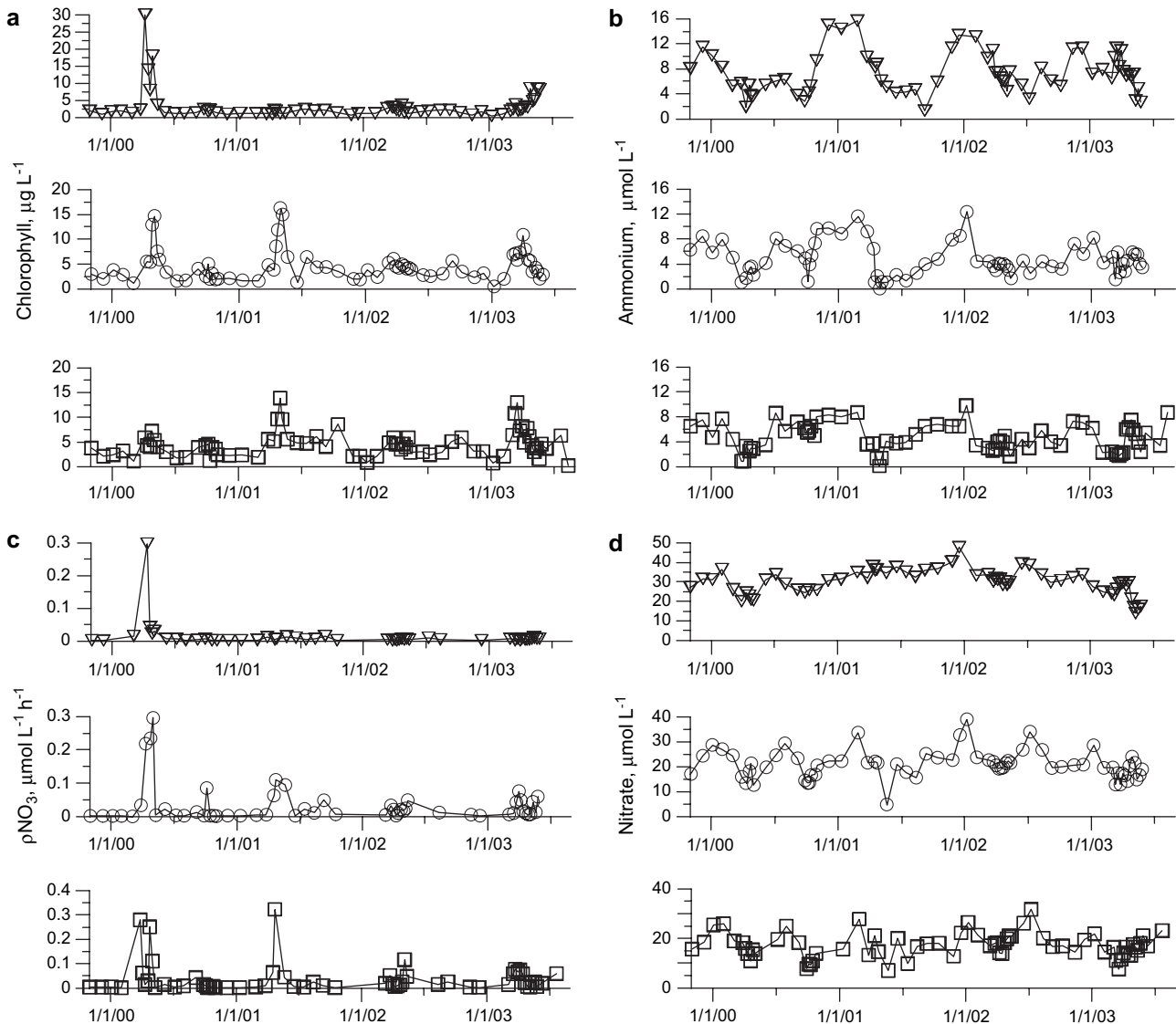


Fig. 1. Surface time series data collected in Suisun (triangles), San Pablo (circles) and Central Bays (squares) from November 1999 to August 2003. (a) Chlorophyll *a*,  $\mu\text{g L}^{-1}$ , (b)  $\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$ , (c) trace  $\rho^{15}\text{NO}_3$ ,  $\mu\text{mol L}^{-1} \text{h}^{-1}$ , (d)  $\text{NO}_3$ ,  $\mu\text{mol L}^{-1}$ .

experiments using water from all three bays. Suisun Bay enclosures show consistently low initial  $\text{NH}_4$  uptake rates (A. Parker, pers. comm.). Figs. 3 and 4 imply that with decreasing  $\text{NH}_4$  concentrations, if  $\text{NO}_3$  is present, a transition from primarily  $\text{NH}_4$ -based N uptake (Fig. 4a) to primarily  $\text{NO}_3$  uptake will begin at about  $4 \mu\text{mol L}^{-1}$   $\text{NH}_4$  increasing rapidly by  $1 \mu\text{mol L}^{-1}$  where inhibition has decreased to 60% (calculated from the exponential fit in Fig. 3) and will end with solely  $\text{NO}_3$  uptake (Fig. 3) when  $\text{NH}_4$  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  $\text{NH}_4$  uptake and predominantly  $\text{NO}_3$  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  $\text{NO}_3$  concentrations  $>20 \mu\text{mol L}^{-1}$  (Fig. 1d),  $\text{NH}_4$  concentrations  $>10 \mu\text{mol L}^{-1}$  and low specific N uptake rates,  $\text{VNH}_4$  and  $\text{VNO}_3$ ,  $<0.005 \text{h}^{-1}$  (Fig. 5a). Chlorophyll was also low,  $<2 \mu\text{g L}^{-1}$  as were  $\rho\text{NH}_4$  and  $\rho\text{NO}_3$ ,  $<0.02 \mu\text{mol L}^{-1} \text{h}^{-1}$  (Fig. 5b). March samples were characterized by an increase in  $\text{VNH}_4$  (Fig. 5a), but no increase in  $\text{VNO}_3$ , an increase in  $\rho\text{NH}_4$ , but not in  $\rho\text{NO}_3$ , (Fig. 5b), an increase in chlorophyll (Fig. 5b) and a decrease in  $\text{NH}_4$  (Fig. 5a). By mid-April,  $\text{NH}_4$  concentration fell to ca.  $<2 \mu\text{mol L}^{-1}$ ,  $\text{VNH}_4$  and  $\rho\text{NH}_4$  decreased to low, February values. However,  $\text{VNO}_3$  increased as did  $\rho\text{NO}_3$  along with chlorophyll concentration that all rose steeply reaching maxima at the time when the sum of  $\rho\text{NH}_4$  and  $\rho\text{NO}_3$  reached a peak (Fig. 5b). Following the peak in chlorophyll,  $\text{NO}_3$  concentration fell to ca.  $5 \mu\text{mol L}^{-1}$  (not shown),  $\text{VNO}_3$  and  $\rho\text{NO}_3$  decreased to reach February values by early June and chlorophyll declined, marking the end of the spring bloom. This same temporal

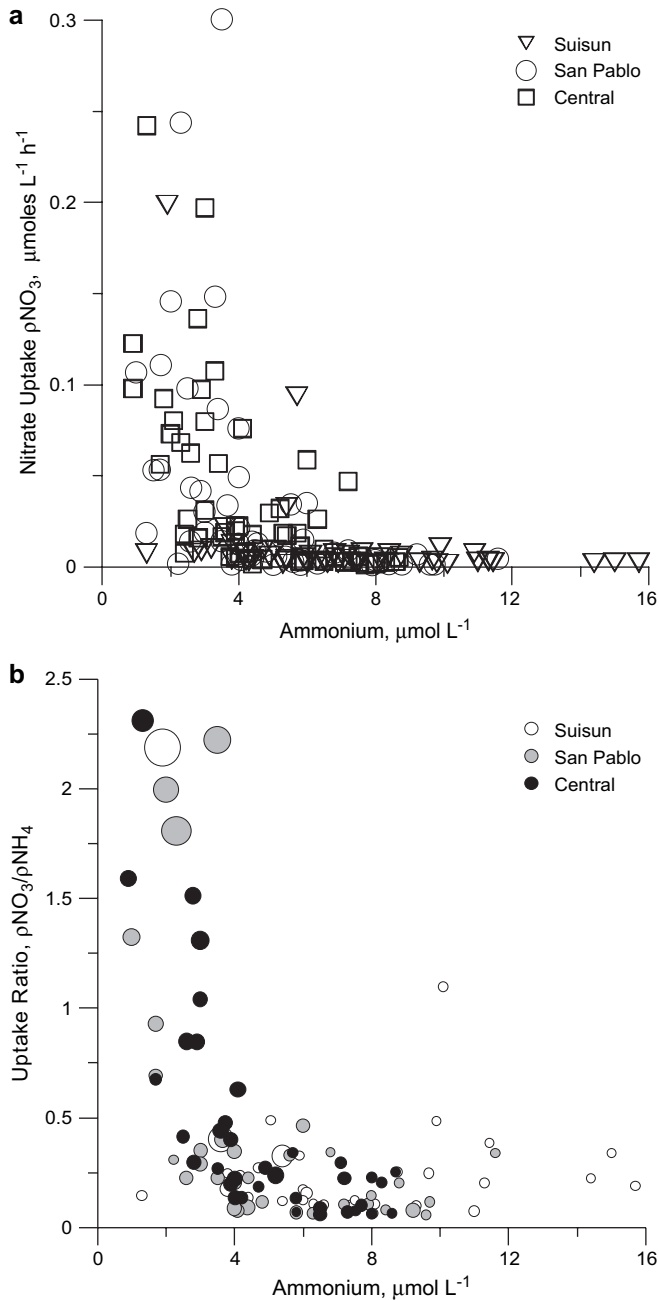


Fig. 2. (a) Saturated  $\rho\text{NO}_3$ ,  $\mu\text{mol L}^{-1} \text{h}^{-1}$  versus  $\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$  for Suisun, San Pablo and Central Bays and (b) ratio of saturated  $\rho\text{NO}_3$  to  $\rho\text{NH}_4$  versus  $\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$ . The points in the graph are shown as bubbles that indicate chlorophyll concentration.

sequence resolved on a better time scale (as weekly samples were available), with rising  $\text{VN}_{\text{H}_4}$ , falling  $\text{NH}_4$  concentration, rising  $\text{VNO}_3$ , and peak values of combined  $\text{NH}_4$  and  $\text{NO}_3$  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  $\text{NH}_4$  and  $\text{NO}_3$ : (1) an increase in  $\text{VN}_{\text{H}_4}$  (presumably the result of improved irradiance/stability conditions) resulting in a small increase in biomass (chlorophyll); (2) as a result of the increase in  $p \text{ NH}_4$  (i.e.  $\text{VN}_{\text{H}_4} \times \text{biomass}$  as particulate

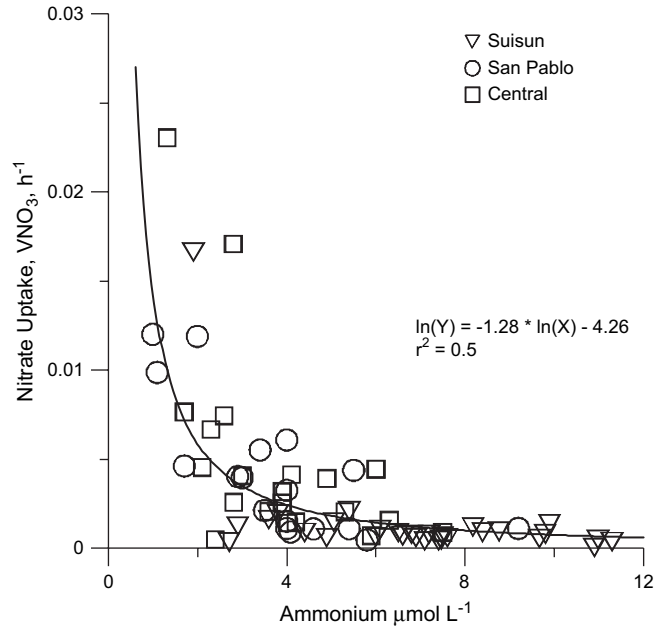


Fig. 3. Trace  $\text{VNO}_3$ ,  $\text{h}^{-1}$  versus  $\text{NH}_4$  concentration,  $\mu\text{mol L}^{-1}$  for the spring bloom periods in Suisun, San Pablo and Central Bays. Exponential line fit through the San Pablo and Central Bay data.

nitrogen, PON), a decrease in  $\text{NH}_4$  concentration occurs to less inhibiting levels for  $\text{NO}_3$  uptake; and then (3)  $\text{VNO}_3$  rises and with an increase in  $\rho\text{NO}_3$  fuels a strong increase in biomass. Although  $\text{VN}_{\text{H}_4}$  has declined to low levels at this stage,  $\rho\text{NH}_4$  remains relatively high due to the high biomass (i.e. low  $\text{VN}_{\text{H}_4} \times \text{high PON} = \text{high } \rho\text{NH}_4$ ). Then (4) a short period of high  $\rho\text{N}_{\text{total}}$  (i.e. sum of  $\rho\text{NO}_3$  and  $\rho\text{NH}_4$ ) occurs as chlorophyll concentration peaks; and (5) finally reduced ambient concentrations of  $\text{NO}_3$  and  $\text{NH}_4$ , no longer support the phytoplankton population and the spring bloom is terminated. There are two transition points or “thresholds” for  $\text{NH}_4$  concentration that need to be distinguished and kept in mind. The first is the  $4 \mu\text{mol L}^{-1}$  value when chlorophyll accumulation based on  $\text{NH}_4$  uptake begins, and the second, about  $1 \mu\text{mol L}^{-1}$   $\text{NH}_4$  when the inhibition effect is reduced to about half maximum (60% according to the curve fit in Fig. 3). Below that value  $\text{NO}_3$  uptake increases steeply with decreased  $\text{NH}_4$  concentrations. Neither of these values should be taken as invariant, but in SFB they are in the expected order,  $\text{NH}_4$  uptake first, then  $\text{NO}_3$ . With favorable irradiance and water column stability, the signature of an oncoming spring bloom is the simultaneous decline in  $\text{VN}_{\text{H}_4}$  and increase in  $\text{VNO}_3$  and a maximum in summed  $\text{NH}_4$  and  $\text{NO}_3$  uptake coinciding with a peak value of chlorophyll. This sequence explains the apparent requirement for  $\text{NO}_3$  uptake for bloom formation, the threshold of ca.  $4 \mu\text{mol L}^{-1}$   $\text{NH}_4$  below which high chlorophyll concentrations develop, and the high ratio of  $\text{NO}_3$  to  $\text{NH}_4$  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

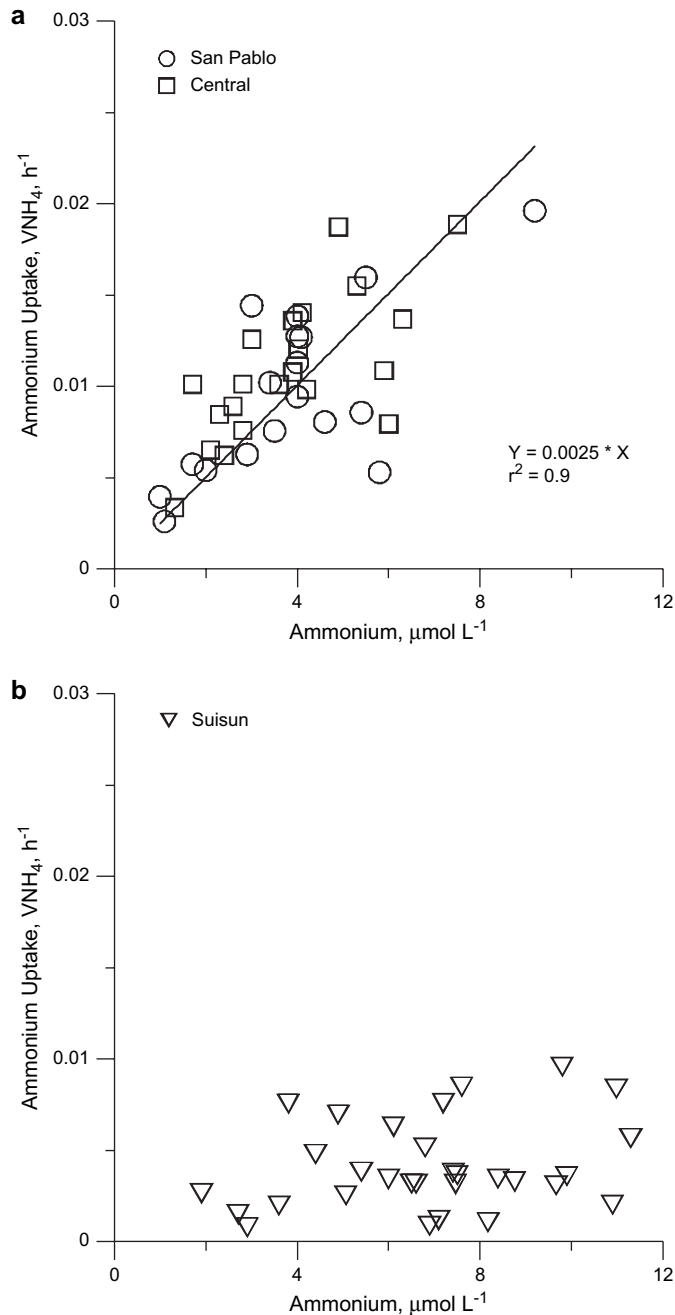


Fig. 4. Trace  $\text{VN}_{\text{H}_4}$ ,  $\text{h}^{-1}$  versus  $\text{NH}_4$  concentration,  $\mu\text{mol L}^{-1}$  for the spring bloom periods in (a) San Pablo and Central Bays, (b) Suisun Bay.

on a daily basis and without the light limitation that results from turbulent mixing in situ. Changes in uptake of  $\text{NH}_4$  and  $\text{NO}_3$  in response to different ambient  $\text{NH}_4$  concentrations were measured in water from Central Bay held in experimental enclosures. Enclosure experiments (Fig. 7a–e) that contained different ambient concentrations of  $\text{NH}_4$  (low ambient  $\text{NH}_4 < 5 \mu\text{mol L}^{-1}$  and higher,  $> 5 \mu\text{mol L}^{-1}$ ) showed depletion of  $\text{NO}_3$  to occur once  $\text{NH}_4$  had been reduced to low levels (Fig. 7a,b). Depletion of  $\text{NO}_3$  began after 1 day in the enclosures with low initial  $\text{NH}_4$  (enclosures A, B; Fig. 7a). In the enclosures (C, D, E, F) with higher initial ambient levels of  $\text{NH}_4$ , there was a lag before  $\text{NO}_3$  was drawn down and  $\text{NO}_3$

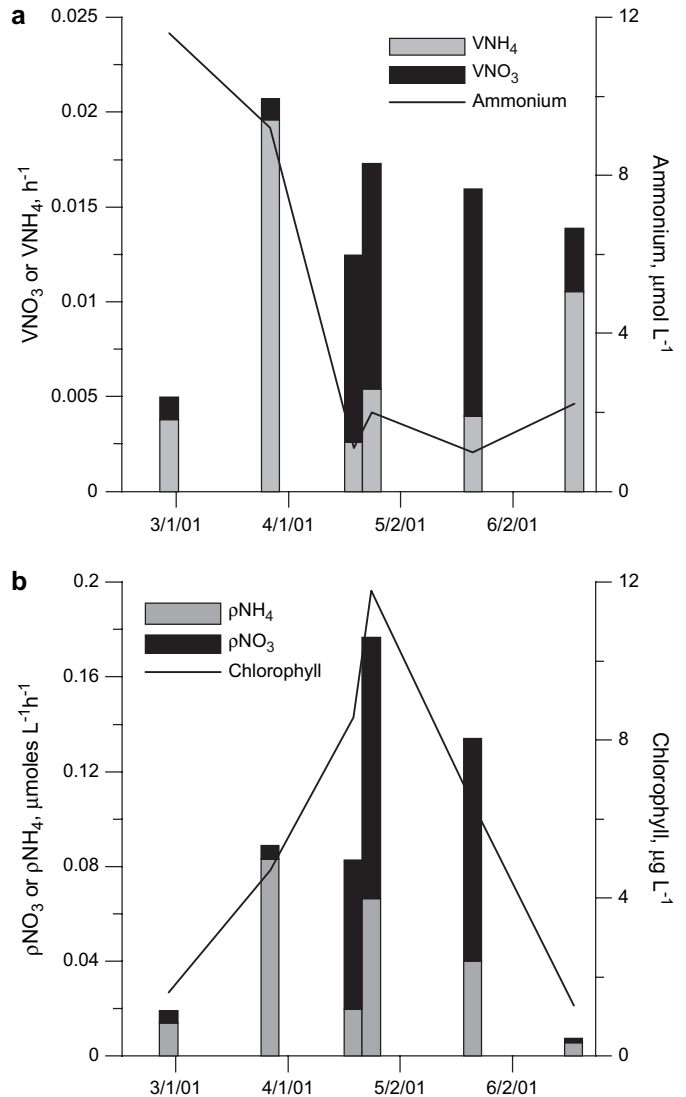


Fig. 5. (a) Trace  $\text{VN}_{\text{H}_4}$ ,  $\text{h}^{-1}$ , trace  $\text{VNO}_3$ ,  $\text{h}^{-1}$  and  $\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$ , (b) trace  $\rho\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$ , trace  $\rho\text{NO}_3$ ,  $\mu\text{mol L}^{-1}$  and chlorophyll concentration,  $\mu\text{g L}^{-1}$  for San Pablo Bay in spring, 2001.  $\text{NO}_3$  concentration at start was  $33.6 \mu\text{mol L}^{-1}$ .

concentrations in the enclosures decreased (Fig. 7b). Maximum  $\text{VNO}_3$  was delayed (Fig. 7c) in most of the enclosures with higher initial  $\text{NH}_4$  (enclosures C, E, F). Maximum specific  $\text{NO}_3$  uptake was reached after 2–3 days (Fig. 7c) depending on the initial concentration of  $\text{NH}_4$ , with values of  $\text{VNO}_3$  exceeding those of  $\text{VN}_{\text{H}_4}$ . There was no change in  $\text{VN}_{\text{H}_4}$  uptake with time in the enclosures (Fig. 7d). Chlorophyll *a* biomass accumulated in all enclosures reaching almost  $30 \mu\text{g L}^{-1}$  (Fig. 7e) supported primarily by  $\text{NO}_3$  (Fig. 7a,b) as calculated by simple mass balance assuming  $1 \mu\text{g}$  chlorophyll *a* generated for  $1 \mu\text{mol N}$  taken up.

The effect of adding more  $\text{NH}_4$  to enclosures to see if  $\text{NO}_3$  uptake was suppressed was investigated in spring 2003 using 20-L enclosures filled with Central Bay water and different experimental additions of  $\text{NH}_4$  (5 to  $30 \mu\text{mol L}^{-1}$ ). Increased  $\text{NH}_4$  concentration resulted in a delay of the onset of  $\text{NO}_3$  uptake, or increased lag time before  $\text{NO}_3$  depletion was observed

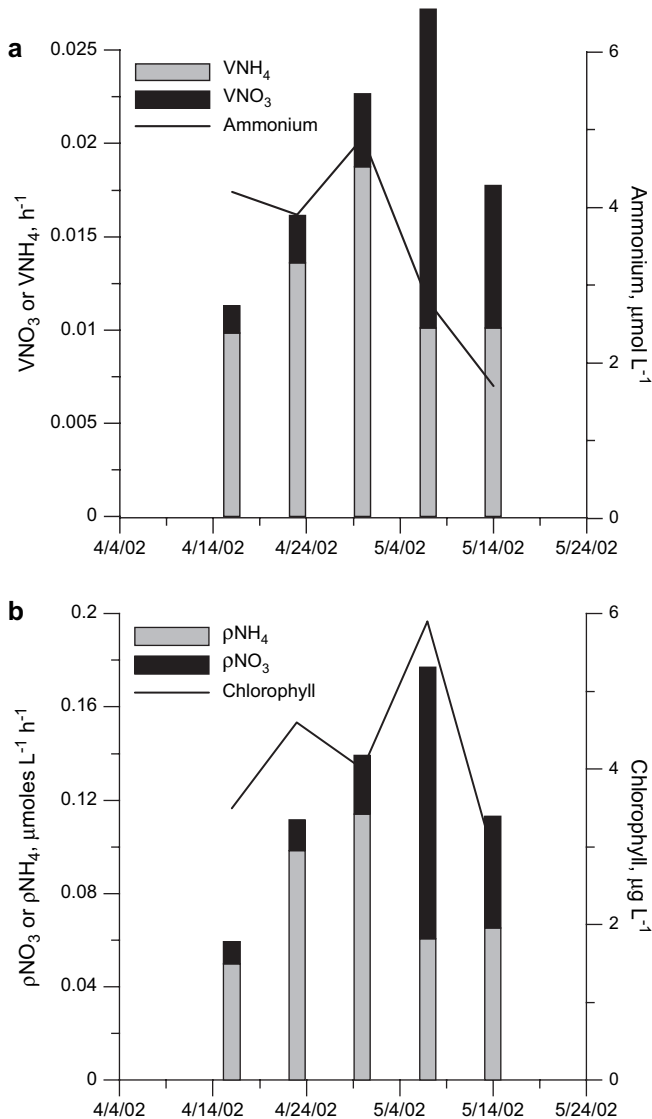


Fig. 6. (a) Trace VNH<sub>4</sub>, h<sup>-1</sup>, trace VNO<sub>3</sub>, h<sup>-1</sup> and NH<sub>4</sub>, μmol L<sup>-1</sup>, (b) trace ρNH<sub>4</sub>, μmol L<sup>-1</sup> h<sup>-1</sup>, trace ρNO<sub>3</sub>, μmol L<sup>-1</sup> h<sup>-1</sup> and chlorophyll concentration, μg L<sup>-1</sup> for Central Bay in spring, 2002. NO<sub>3</sub> concentration at start was 14 μmol L<sup>-1</sup>.

(Fig. 8a). The enclosure with no experimental addition had an initial NH<sub>4</sub> concentration of 5.7 μmol L<sup>-1</sup> and required 2 days to reduce the NH<sub>4</sub> concentration to a low value (0.8 μmol L<sup>-1</sup>; Fig. 8b), at which point NO<sub>3</sub> decreased in the enclosure (Fig. 8a). At the highest addition, 30 μmol L<sup>-1</sup>, no NO<sub>3</sub> decrease was observed during the 4 days of the experiment. When the values of VNO<sub>3</sub> from the different sets of additions were combined for all 4 days of the experiment and plotted versus the NH<sub>4</sub> concentration at the sampling time of the uptake measurement (Fig. 8c), high values of VNO<sub>3</sub> appear only at low NH<sub>4</sub> concentrations, ca. 1 μmol L<sup>-1</sup>. At higher NH<sub>4</sub> concentrations VNO<sub>3</sub> 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 VNO<sub>3</sub> to VNH<sub>4</sub> (Fig. 8d), at low NH<sub>4</sub> concentrations shows the same pattern as seen for the uptake ratio in the three bays

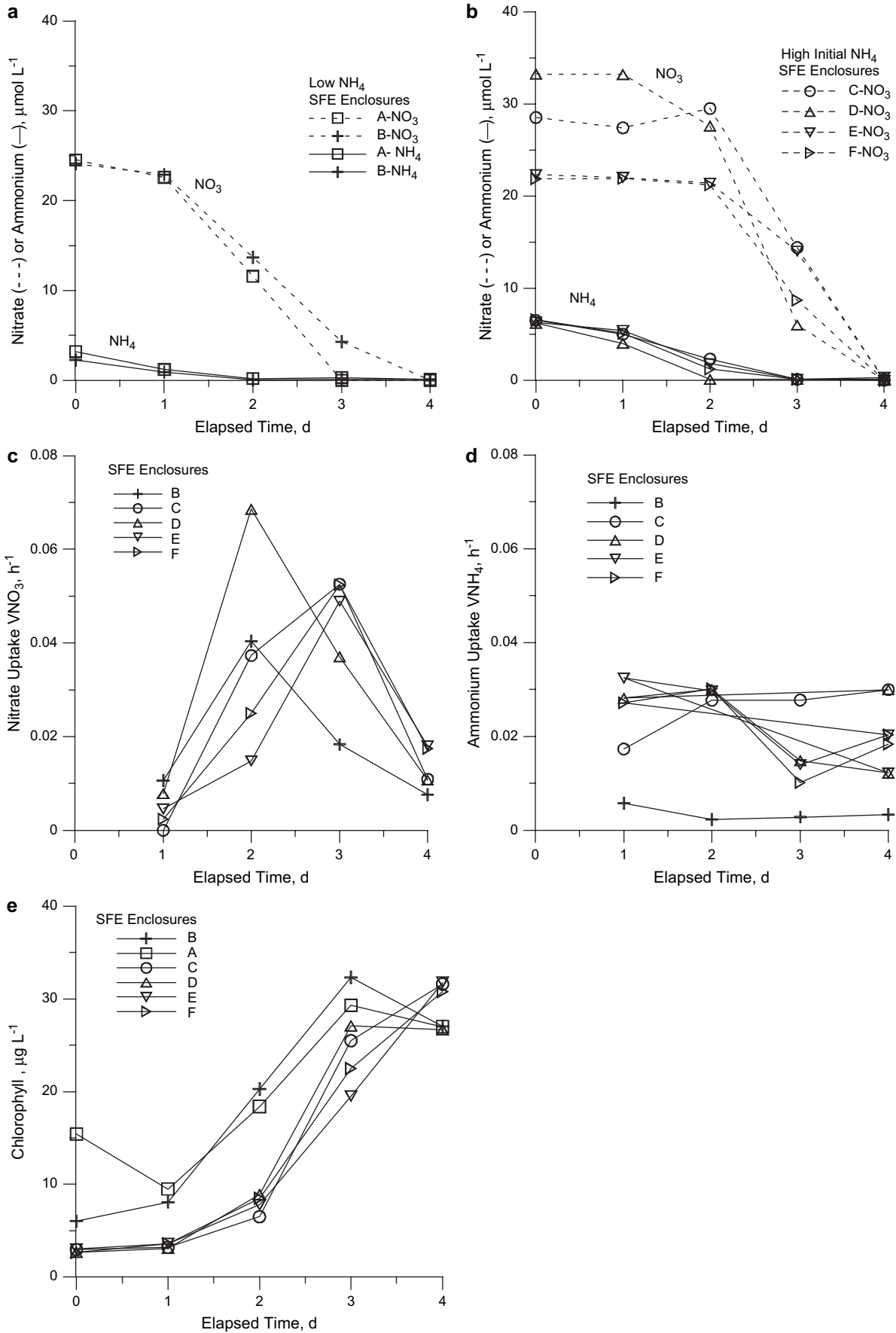
(Fig. 2b). These results demonstrate that the NH<sub>4</sub> inhibition effects apparent in the bay can be experimentally reproduced by the addition of NH<sub>4</sub> to SFB water, i.e. a direct demonstration of NH<sub>4</sub> inhibition of NO<sub>3</sub> uptake in bay water.

## 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 NO<sub>3</sub> concentrations in the estuary are generally unavailable to the phytoplankton due to the presence of NH<sub>4</sub>.

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 NH<sub>4</sub> accumulate due to continuing inputs and low phytoplankton nutrient uptake activity. In spring, increases in seasonal irradiance create favorable conditions for phytoplankton growth and NH<sub>4</sub> 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 NH<sub>4</sub> uptake (Fig. 5b). If the combination of these processes results in NH<sub>4</sub> concentrations being reduced to below 4 μmol L<sup>-1</sup> to a value of about 1 μmol L<sup>-1</sup> (Fig. 3), NO<sub>3</sub> 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 NH<sub>4</sub> and the higher ambient concentration of NO<sub>3</sub>. Mass balance considerations indicate that to obtain the concentrations of chlorophyll measured in SFB, ambient NH<sub>4</sub> is insufficient and NO<sub>3</sub> must be used also. If NO<sub>3</sub> uptake is not turned on, the biomass increase is small and limited to the amount of NH<sub>4</sub> taken up. In years with insufficient dilution, and higher levels of NH<sub>4</sub> (i.e. >4 μmol L<sup>-1</sup>) 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 NH<sub>4</sub> and regeneration of the bloom-produced organic nitrogen by grazing or by bacterial action at the sediment surface (Caffrey, 1995) results in NH<sub>4</sub> concentrations returning to levels inhibiting NO<sub>3</sub> uptake. Similar observations have been described for Delaware Bay (Sharp et al., 1984; Pennock and Sharp, 1994; Yoshiyama and Sharp, 2006) with





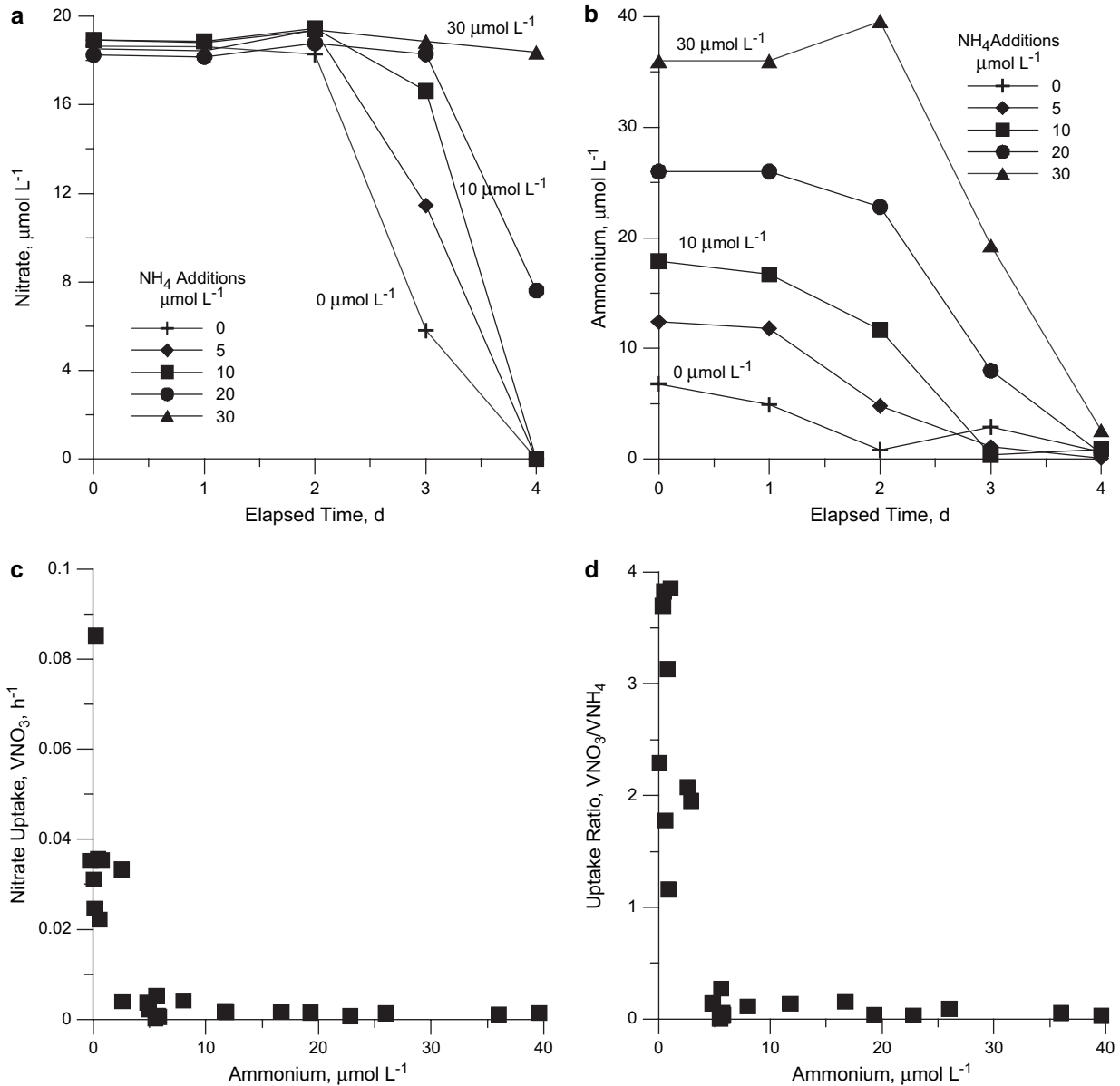


Fig. 8. Results from enclosures filled with Central Bay water in spring 2003 treated with  $\text{NH}_4$  additions of 0, 5, 10, 20, 30  $\mu\text{mol L}^{-1}$  and followed for 4 days. (a)  $\text{NO}_3$ ,  $\mu\text{mol L}^{-1}$ , (b)  $\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$  plotted against elapsed time, (c) trace  $\text{VNO}_3$ ,  $\text{h}^{-1}$ , (d) ratio of trace  $\text{VNO}_3:\text{VN}\text{H}_4$  plotted against the  $\text{NH}_4$ ,  $\mu\text{mol L}^{-1}$  at the sampling time of the uptake measurement.

spring blooms initiated by  $\text{NH}_4$ , and after exhaustion of  $\text{NH}_4$  significant uptake of  $\text{NO}_3$ , that is followed by a return in summer to the use of  $\text{NH}_4$ .

#### 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  $\text{NH}_4$  concentration to values allowing  $\text{NO}_3$  uptake to take place. The time required to reduce  $\text{NH}_4$

concentrations, from the typical high levels in SFB, to reduced inhibitory levels for  $\text{NO}_3$  uptake (i.e. to about 50% inhibition at 1  $\mu\text{mol L}^{-1}$   $\text{NH}_4$ ) 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  $\rho\text{NH}_4$  is the measured mean  $\rho\text{NH}_4$  value. Values calculated from Eq. (1) using the seasonal mean  $\text{NH}_4$  concentrations and  $\text{NH}_4$  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  $\text{NH}_4$  (enclosures C, D, E, F); all frames show results against elapsed time up to 4 days. (a)  $\text{NO}_3$  and  $\text{NH}_4$  concentration,  $\mu\text{mol L}^{-1}$  in enclosures A and B (low  $\text{NH}_4$ ), (b)  $\text{NO}_3$  and  $\text{NH}_4$  concentrations,  $\mu\text{mol L}^{-1}$  in enclosures C–F (high  $\text{NH}_4$ ), (c) trace  $\text{VNO}_3$ ,  $\text{h}^{-1}$ , (d) trace  $\text{VN}\text{H}_4$ ,  $\text{h}^{-1}$  versus elapsed time in enclosures B through F. No  $^{15}\text{N}$  data are available for enclosure A. (e) Chlorophyll concentration ( $\mu\text{g L}^{-1}$ ) 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  $\text{NH}_4$  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  $1 \mu\text{mol L}^{-1}$ ) are just below 3 days for each bay. In summer, the unfavorable times for depletion of  $\text{NH}_4$  in San Pablo and Central Bays, 8.5 and 8.4 days, respectively, are due largely to the almost 2-fold decrease in mean  $\text{NH}_4$  uptake in summer. Unfavorable conditions in Suisun Bay for both seasons, 15 days in spring and 9.6 days in summer for  $\text{NH}_4$  to reach  $1 \mu\text{mol L}^{-1}$ , are due to both low  $\text{NH}_4$  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  $\text{NH}_4$  concentrations. The reason for this low  $\text{NH}_4$  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  $\text{NH}_4$  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  $\text{NH}_4$  uptake. It is likely that after 1 or 2 days of good irradiance/stability conditions, the  $\text{NH}_4$  uptake rate would increase above the mean value and shorten the time to reach  $1 \mu\text{mol L}^{-1}$   $\text{NH}_4$ , when high rates of  $\text{NO}_3$  uptake would occur. In enclosure experiments,  $\text{NH}_4$  uptake rates increased with time and resulted in rapid reduction in  $\text{NH}_4$  to zero in 2–3 days in the enclosure experiments. Besides time to reduce ambient  $\text{NH}_4$  to non-inhibitory levels, bloom formation also requires more time with sufficient light for  $\text{NO}_3$  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  $\text{NH}_4$ , 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  $32 \mu\text{g L}^{-1}$  by day 6 of a neap tide cycle.

#### 4.3. Consequences of high $\text{NH}_4$ loading

$\text{NH}_4$  inhibition of  $\text{NO}_3$  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  $\text{NH}_4$  in San Pablo Bay in winter is  $8 \mu\text{mol L}^{-1}$  and that of  $\text{NO}_3$  is  $26.9 \mu\text{mol L}^{-1}$  (Wilkerson et al., 2006). If chlorophyll were to be produced in a spring bloom equally by consuming either  $\text{NH}_4$  at  $8 \mu\text{mol L}^{-1}$  or  $\text{NO}_3$  at  $26.8 \mu\text{mol L}^{-1}$ , an  $\text{NO}_3$ -based bloom would produce ca. 3.4 times as much chlorophyll as one based on  $\text{NH}_4$  alone; or if both sources were fully utilized, the resulting chlorophyll would be 4.4 times that of an  $\text{NH}_4$ -only bloom.

The potential effect of  $\text{NH}_4$  inhibition of  $\text{NO}_3$  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 ( $\text{PO}_4$ ) or silicate ( $\text{Si}(\text{OH})_4$ ) limited system. However, if substantial  $\text{NH}_4$  is present ( $>4 \mu\text{mol L}^{-1}$ ) then  $\text{NO}_3$  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),  $\text{Si}(\text{OH})_4 = 73.0 \mu\text{mol L}^{-1}$ ,  $\text{NO}_3 = 20.7 \mu\text{mol L}^{-1}$ ,  $\text{NH}_4 = 4.9 \mu\text{mol L}^{-1}$ ,  $\text{PO}_4 = 2.9 \mu\text{mol L}^{-1}$ , Central Bay is clearly N limited (with a ratio of P to available DIN of 1:1.7), despite the presence of considerable  $\text{NO}_3$ . The Central Bay primary production ecosystem is likely regulating in summer on  $\text{NH}_4$  through a combination of inputs from anthropogenic sources, by regeneration at the sediment surface and by grazing. The quasi-steady state concentration of  $\text{NH}_4$  makes the  $\text{NO}_3$  pool invisible to the ecosystem.

Irradiance and physical conditions are important in determining the outcome of  $\text{NH}_4$  inhibition on productivity. In other estuaries with irradiance conditions that are favorable for long periods of time (unlike SFB) accompanied by high  $\text{NH}_4$  inputs, blooms of the type described for SFB will occur more regularly as a result of sufficient light and drawdown of  $\text{NH}_4$  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  $20 \mu\text{g L}^{-1}$ .  $\text{NH}_4$  concentrations can be as high as  $10 \mu\text{mol L}^{-1}$  but appear to be drawn down to a range 0.1 to  $1 \mu\text{mol L}^{-1}$  that allows access to  $\text{NO}_3$  which is drawn down from 10 to  $0 \mu\text{mol L}^{-1}$ , with accompanying increase in chlorophyll of up to  $20 \mu\text{g L}^{-1}$ ; values that would require the sum of  $\text{NO}_3$  and  $\text{NH}_4$  uptake to occur.

Table 1  
Days to deplete ambient  $\text{NH}_4$  to  $1 \mu\text{mol L}^{-1}$  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 $1 \mu\text{mol L}^{-1}$	Mean $\text{NH}_4$ ( $\mu\text{mol L}^{-1}$ )	Mean $\rho\text{NH}_4$ ( $\text{nmol L}^{-1} \text{h}^{-1}$ )	Days to $1 \mu\text{mol L}^{-1}$	Mean $\text{NH}_4$ ( $\mu\text{mol L}^{-1}$ )	Mean $\rho\text{NH}_4$ ( $\text{nmol L}^{-1} \text{h}^{-1}$ )
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  $\text{NH}_4$  (Paerl, 1999). An understanding of the critical role of anthropogenic  $\text{NH}_4$  input could provide a powerful tool for management of estuarine productivity, since typically the proportion of the anthropogenic input/loading of  $\text{NH}_4$  in these regions can be controlled by changes in water treatment practices and water allocation (dilution). Some agricultural practices could be modified to reduce  $\text{NH}_4$  inputs as well. Regulating  $\text{NH}_4$  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  $\text{NH}_4$  to  $\text{NO}_3$  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  $\text{NH}_4$  on bloom formation. The basic pattern of  $\text{NH}_4$  distribution in SFB in winter is the result of mixing between water with high  $\text{NH}_4$  and low salinity at the head of the estuary, and low  $\text{NH}_4$  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  $\text{NH}_4$  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  $\text{NH}_4$  remains high or is increased and up to 80% of the  $\text{NH}_4$  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  $13 \mu\text{g L}^{-1}$  to  $7 \mu\text{g L}^{-1}$  from 1978 to 1986 (Fig. 5 in Alpine and Cloern, 1992) suggesting some other causal factor, possibly increased  $\text{NH}_4$  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  $\text{NH}_4$ . 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  $\text{NO}_3$  in two ways, by holding chlorophyll levels too low to reduce  $\text{NH}_4$  to non-inhibitory levels, and by regenerating a portion of the assimilated nitrogen and contributing to the ambient  $\text{NH}_4$  pool. The effect of the clams in Suisun Bay impacts the seaward bays (San Pablo and Central Bays) as well with more  $\text{NH}_4$  exported southward than would be the case if the Suisun phytoplankton were able to process riverine  $\text{NH}_4$  more effectively. In effect, the net retention of  $\text{NH}_4$  in Suisun Bay is currently low, since phytoplankton are growing solely on  $\text{NH}_4$  at a low rate, and the clams are regenerating a portion of productivity as  $\text{NH}_4$  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  $\text{NH}_4$  inputs may have been lower at that time, opening the window for  $\text{NO}_3$  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,  $\text{NH}_4$  probably increased in the early 1980s, when waste water dischargers were required to add basic secondary treatment, converting organic nitrogen to  $\text{NH}_4$  (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  $\text{NH}_4$  inhibition of  $\text{NO}_3$  uptake and chlorophyll accumulation. We suspect other U.S. estuarine ecosystems, may be impacted by increased inputs of  $\text{NH}_4$ . 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  $\text{NH}_4$ , 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  $\text{NH}_4$  inputs and concentrations that can suppress access to  $\text{NO}_3$  by phytoplankton and may reduce the occurrence of spring blooms and quantity of accumulated chlorophyll. Since the  $\text{NH}_4$  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  $\text{NH}_4$ . 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.

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