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Nutrient Fluxes from Sediments in the San Francisco Bay Delta

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Abstract In September 2011 and March 2012, benthic nutrient fluxes were measured in the San Francisco Bay Delta, across a gradient from above the confluence of the Sacramento and San Joaquin Rivers to Suisun Bay. Dark and illuminated core incubation techniques were used to measure rates of denitrification, nutrient fluxes (phosphate, ammonium, nitrate), and oxygen fluxes. While benthic nutrient fluxes have been assessed at several sites in northern San Francisco Bay, such data across a Delta–Bay transect have not previously been determined. Average September rates of DIN (nitrate, nitrite, ammonium) flux were net positive across all sites, while March DIN flux indicated net uptake of DIN at some sites. Denitrification rates based on the N_2/Ar ratio approach were between 0.6 and 1.0 mmol m^{-2} day^{-1}, similar to other mesotrophic estuarine sediments. Coupled nitrification–denitrification was the dominant denitrification pathway in September, with higher overlying water nitrate concentrations in March resulting in denitrification driven by nitrate flux into the sediments. Estimated benthic microalgal productivity was variable and surprisingly high in Delta sediments and may represent a major source of labile carbon to this ecosystem. Variable N/P stoichiometry was observed in these sediments, with deviations from Redfield driven by processes such as denitrification, variable light/dark uptake of nutrients by microalgae, and adsorption of soluble reactive phosphorus.

Keywords Benthic flux · Denitrification · Nutrient stoichiometry · N/P ratios · P efflux · Benthic microalgae

Introduction

Management issues related to the San Francisco Bay Delta are complex. Many management questions and actions are directly affected by the extent to which the factors contributing to food web changes can be identified and managed. Several fish, including the delta smelt (*Hypomesus transpacificus*) and longfin smelt (*Spirinchus thaleichthys*), are on the federal endangered species list or are considered threatened (Wanger 2007a, b). Water exports have been restricted by court order in recent years in an attempt to restore these species; new habitat is being created with the hope that it will contribute positively to the restoration of the system; and proposed major re-engineering of the flow is also being debated (e.g., Bay Delta Conservation Plan, 2010, http://baydeltaconservationplan.com/BDCPPlanningProcess/ReadDraftPlan/ReadDraftPlan_copy1.aspx).

Nutrient cycling bears on these issues in multiple ways. The estuary has been considered to have chronically low rates of productivity (e.g., Jassby et al. 2002; Kimmerer et al. 2012). Nutrient loads, speciation, and stoichiometry affect productivity and phytoplankton composition and ultimately can alter trophodynamics (e.g., Berg et al. 2001; Kemp et al. 2005; Glibert 2010, 2012; Glibert et al. 2011; Parker et al. 2012). While impacts of nutrients have long been ignored in this system compared to other stressors such as invasive bivalves (Alpine and Cloern 1992; Greene et al. 2011), nutrients are now gaining attention as important ecosystem stressors (Dugdale et al. 2007; van Nieuwenhuyse 2007; Jassby 2008; Glibert 2010, 2012; Glibert et al. 2011; Parker et al. 2012). Nutrients loads have increased substantially over the past decades due to increased sewage effluent loads (Van Nieuwenhuyse 2007; Dugdale et al. 2007; Glibert et al. 2011). Yet, despite the increasing recognition of nutrients as a potential stressor for this system, an accurate accounting of nutrient sources and sinks in the Bay Delta is not available. Without consideration of the role of nutrient sources and fluxes, the

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potential success of restoration of habitat restoration for native species will likely remain unpredictable.

Sediments are key components of shallow water estuarine ecosystems, both responding to changing environmental conditions and, at the same time, modifying the chemistry of the overlying water column. The role of sediments as "sinks" of contaminants, organic matter, and nutrients has been studied for decades, and their role as nutrient transformers has been well described. Sediments can be sinks for nutrients via burial and microbial denitrification and via assimilation into benthic algae and rooted macrophytes (Joye and Anderson 2008; Lehtoranta et al. 2009). Conversely, sediments are also sources of remineralized nutrients to support water column primary production. Sediments recycle fixed nitrogen (N) and phosphorus (P) to the water column at rates that do not necessarily reflect their rates of deposition. Remineralized N can be returned to the water column as fixed N (NH_4^+ or NO_x) or as N_2 after the process of denitrification. Phosphorus can be returned to the water column as soluble reactive P (SRP, essentially equivalent to PO_4^{3-}) or retained within the sediments as both inorganic (mineral or adsorbed) and organic P. Rates of sediment–water exchange of nutrients can be affected by a large number of factors, including input rates of labile C, N, and P; presence/absence of dissolved O_2 in overlying water (Mortimer 1971; Rysgaard et al. 1994; Kemp et al. 2005); salinity (Caraco et al. 1990; Gardner et al. 1991); availability of terminal electron acceptors including NO_3^-, Mn(IV), Fe(III), and SO_4^{2-} (Anderson 1982; Cornwell et al. 1999; Lehtoranta et al. 2009); activity of bioturbating and bioirrigating animals (Aller 1980; Pelegri et al. 1994; Owens 2009); and pH (Seitzinger 1991; Glibert et al. 2011; Gao et al. 2012). The relative importance of sediment processes to the biogeochemistry of coastal systems is inversely related to the depth of the water column and directly related to the residence time of the water within the system (Nixon et al. 1996).

In systems in which P loading has been reduced from point source effluent or detergents, as occurred in the 1990s in the Bay Delta (Van Nieuwenhuyse 2007; Glibert 2010; Glibert et al. 2011), sediments can become the major source of this important macronutrient. In non-calcareous freshwater sediments, P is most often bound to iron oxyhydroxides (FeOOH; Williams et al. 1971; Jordan et al. 2008). The FeOOH-bound P may be delivered to estuaries with transport of suspended solids or may become adsorbed to particulates when P is discharged from other sources, such as from point source discharges. When this bound P meets saline or sulfate-rich water, either from transport down-estuary or from salt intrusion to sediments, formation of iron sulfide minerals can release P to overlying water (Caraco et al. 1990; Jordan et al. 2008; Lehtoranta et al. 2009). In the Bay Delta strong salinity gradients, shallow water depths and variable amounts of primary production/algal biomass are expected to have an important effect on sediment nutrient recycling (as in other coastal ecosystems; Boynton and Kemp 2008). Prior to this study, few measurements of sediment nutrient dynamics in the Bay Delta have been made (Caffrey 1995; Kuwabara et al. 2009).

Here, we report on a series of measurements of N (NH_4^+, NO_3^-, N_2–N) and P (soluble reactive P or SRP) fluxes from sites encompassing the salinity gradient in the Bay Delta region (e.g., Jassby et al. 1995). Our observations were conducted under high flow conditions in fall 2011 and in spring 2012. We hypothesized that fluxes of N from the sediment to the water column would be higher in late summer than in spring, that site differences would vary with N form, and that N/P stoichiometry of the fluxes would differ from Suisun Bay to upper Delta sites. We also hypothesized that shallow sediments in this system would be sites of considerable benthic productivity.

Methodology

Sampling and Experimentation

Sampling included a transect of 12 sites during each of two seasons, from the flooded islands above the confluence of the Sacramento and San Joaquin Rivers in the Bay Delta to Suisun Bay (Table 1, Fig. 1). Sediments were collected in "Delta" environments (including Mildred's Island, Franks Tract, Big Break, and Sherman Island) on September 14, 2011 and March 15, 2012, and in "Bay" environments (including Browns, Honker, Grizzly, and Suisun Bays) on September 16, 2011 and March 17, 2012. Each site was sampled in duplicate, except for Big Break in 2012, when six cores were collected from that site. An aluminum pole corer was used for sediment collection in the generally shallow deltaic environments, using 7 cm id acrylic cores with a sediment depth of 15 cm. In the Bay environments, both the pole corer and a Soutar-designed non-metallic box corer were used. Sub-cores were inserted into the box corer at each site. Although undisturbed cores were collected at all sites, both sampling approaches had limitations: (1) the pole corer was able to collect samples to a water column depth of ~3 m, making core collection at Mildred's Island limited to a shallower water site on the northern edge, and (2) the box corer did not have sufficient penetration power at some deeper water sites, limiting sampling to shallow water sites.

At each site, the station location was recorded using GPS; photosynthetically active radiation (PAR) from both the water surface and the sediment surface was recorded using a 2π LiCor light sensor, and salinity and temperature were measured using either YSI sondes or a Sea Bird CTD (selected bay sites only). At each site water was collected using rosette-mounted water sampling bottles or by direct submersion of carboys at the shallow water sites for use in subsequent incubations as described below.

Table 1 Site locations, salinity, temperature, and depth for sampling transect

Site	Latitude	Longitude	Salinity		Temperature		Depth
	N	W	September 11	March 12	September 11 °C	March 12	m
Mildred Island	37.9975	121.5229	0.1	0.2	22.2	13.3	2.5
Franks Tract I	38.0557	121.5886	0.1	0.2	21.6	12.8	1.1
Franks Tract II	38.0262	121.6085	0.1	0.2	22.2	12.8	3.1
Big Break	38.0221	121.7201	0.1	0.2	21.5	13.1	2.0
Sherman Island I	38.0470	121.7918	0.2	0.4	21.3	12.7	1.7
Sherman Island II	38.0452	121.8003	0.2	0.4	20.9	12.9	1.7
Brown	38.0442	121.8739	0.4	2.7	20.8	12.7	2.0
Honker I	38.0733	121.9230	0.9	2.7	19.8	12.6	3.1
Honker II	38.0715	121.9338	1.2	2.7	19.3	12.7	2.0
Grizzly	38.1175	122.0397	3.4	6.0	19.0	12.5	3.1
Suisun I	38.0555	122.1200	8.3	10.2	19.7	12.3	3.0
Suisun II	38.0915	122.0583	5.5	8.4	19.5	12.3	3.2

The 2011 samples were collected on September 14, 2011 and September 16, 2011. The 2012 samples were collected on March 15, 2012 and March 17, 2012

Cores were shaded and kept in a water-filled cooler until transport to the Romberg Tiburon Center, Tiburon, CA, where the experiments were conducted. Upon return to the laboratory, each sediment core was bathed overnight in the overlying water from the respective site. A water-only control core was added to provide an estimate of water column effects on net fluxes. The cores were completely flushed to maintain O_2 saturation, and the overnight pre-incubation allowed the cores time to come to a thermal equilibrium and to equilibrate the N_2, O_2, and Ar in the plastics with the water column.

To initialize flux experiments, a spinning top was installed on each core. All cores were then incubated in 5–7 h of darkness, followed, for a subset of the cores, by a 2–3-h illuminated period using natural sunlight. Dark-only experiments were conducted on those cores that were collected from naturally turbid waters receiving little to no light at the sediment surface. Light incubations were added only for those cores collected from shallower sites that could receive light at the sediment surface. Dark incubation times were chosen to provide sufficient signal for nutrient concentration changes

Fig. 1 Location map for San Francisco Bay Delta and enlarged map illustrating sampling sites for sediment flux work conducted during September 2011 and March 2012. Herein, we consider the Suisun I to Browns set of six sites to be "Bay" sites and the Sherman Island to Mildred's Island sites to be "Delta" sites

without depletion of O_2 below ~75 % of saturation. Light incubation times were sufficient to measure changes without O_2 supersaturation. Neutral density screening was used with natural sunlight to match the irradiances observed in the field (typically PAR values of 50–300 μmol m^{-2} s^{-1}). During the March sediment incubations, heavy rains required that the incubations were carried out inside the SAV greenhouse area at the Tiburon Center; dark overcast conditions resulted in variable light levels.

Cores were sampled seven times during the incubation period, three times in the dark, once at the light/dark transition, and three times in the light, yielding a four-point time series for dark conditions and four-point time series for illuminated conditions. At each time point, samples of the overlying water were collected for dissolved O_2, N_2, argon (Ar), SRP, NH_4^+, and NO_3^-+NO_2^- (also referred to as NO_x). Samples for gas analysis of N_2, O_2, and Ar were collected in 7 mL glass stoppered vials with 10 μL of 50 % saturated $HgCl_2$ added for preservation. Samples for nutrient analysis were collected in syringes, filtered (0.4 μm polycarbonate filter), and frozen until analysis.

At the end of the incubation, the water volume overlying the sediments was measured and triplicated; samples for chlorophyll *a* analysis were sub-cored from the surface 0–1 cm of each core using a cut-off syringe. Chlorophyll *a* samples were immediately frozen to −20 °C.

Analytical Methodology

Membrane inlet mass spectrometry (MIMS) was used for analysis of O_2, N_2, and Ar (Kana et al. 1994). MIMS samples were analyzed by pumping the water through a membrane tube situated inside the mass spectrometer vacuum. Gas ratios (e.g., N_2/Ar) were measured with a precision of <0.03 % c.v. with minimal corrections for O_2 depletion (Kana and Weiss 2004). Argon-normalized gas ratios were converted to gas concentrations using air equilibrated standards. Replicate analyses on the initial sampling (i.e., time zero) from each core were conducted.

Nutrient analysis was conducted using standard automated analysis techniques, with NO_x measured with Cd reduction. Chlorophyll *a* was determined using acetone extraction according to Van Heukelem et al. (1994). These analyses were all carried out with ~10 % replication.

Data Calculations

Sediment–water exchange rates were calculated from the slope of the change of chemical constituent concentrations in the overlying water:

$$F = \frac{\Delta C}{\Delta t} \times \frac{V}{A}$$

where F is the flux (micromoles per square meter per hour), $\Delta C/\Delta t$ is the slope of the concentration change in overlying water (micromoles per liter per hour), V is the volume of the overlying water (liters), and A is the area of the incubated core (per square meter). When the water-only control core had a significant slope, the slope of the flux cores was adjusted accordingly. Daily rates of nutrient exchange for the dark only conditions in Bay sediments were calculated by multiplying dark rates of flux by 24 h; for Delta cores with illuminated time periods, the appropriate light/dark flux estimate was multiplied by the light/dark period length and summed.

Benthic Microalgal Productivity Calculations

The production of benthic microalgae was determined as the difference in O_2 fluxes under illuminated and under dark incubation conditions. This implies that the rates of dark O_2 flux represent a true measure of respiration and that dark and light rates of heterotrophic respiration are the same. Temporal changes in the depth distribution of redox processes resulting from diel changes in O_2 penetration may affect net effluxes during changes from dark to light conditions (Hochard et al. 2010), though comparison of O_2-based benthic microalgal photosynthesis to CO_2-based estimates have shown good agreement (Newell et al. 2002). Daily rates of benthic microalgal production were calculated as the product of the photosynthetic rate and day length.

The variability between duplicate core flux rates differed for the analytes and was assessed as a coefficient of variability (COV) using half the range between cores divided by the absolute value of the average flux rate. Median O_2 and N_2–N duplicate core variability was 12 % for rates less than −500 and 40 μmol m^{-2} h^{-1}, respectively, increasing three- to fivefold for slower rates. Median SRP, NO_x, and NH_4^+ COVs ranged from 31 to 34 % for absolute value rates greater than 10, 20, and 40 μmol m^{-2} h^{-1} respectively, increasing more than threefold for lower rates.

Statistical Tests

A two-way analysis of variance was carried out on the flux and sediment chlorophyll *a* data using the Sigmaplot statistical package (Version 11, Systat Software, Inc.). Under dark conditions, comparisons were made for each parameter, examining the data for differences between Delta and Bay environments, and March and September time periods. For the illuminated Delta sediments, we compared dark versus light conditions. Significance was accepted for $P<0.05$.

Results

Ambient Environmental Conditions

The sampled sites encompassed regions from <1 to 10.2 salinity (Table 1). All sites had depths≤3.2 m at the time of sampling. Temperatures varied across sites by up to 3.2 °C in September (19.5–22.2 °C), but a much smaller temperature gradient (12.3–13.3 °C) across sites was observed in March (Table 1). September concentrations of NO_x were <5 μmol L^{-1} in Delta sites other than Sherman Lake, while Sherman Lake and Bay concentrations were 17–22 μmol L^{-1}. In March, all Bay and Delta sites had NO_x concentrations of 40–43 μmol L^{-1}.

Nitrogen Fluxes

With few exceptions, virtually all cores from all sites, both Delta and Bay, exhibited net effluxes of N_2–N or denitrification (Fig. 2). The dark N_2–N fluxes averaged 34±30 μmol m^{-2} h^{-1} with a median of 32 μmol m^{-2} h^{-1} in September and 48±31 μmol m^{-2} h^{-1} with a median rate of 48 μmol m^{-2} h^{-1} in March; these temporal differences were not significant (see ANOVA results in Table 2). The Bay denitrification rates were significantly lower ($P<0.05$) than Delta rates, and within the Delta, dark rates were significantly ($P<0.05$) greater than light rates.

Fluxes of NO_x were generally directed into the sediments in March and out of the sediment during September (Fig. 3). Spatially, most of the sites in the Delta (Sherman Island excepted) had NO_x fluxes directed into the sediments during both seasons, whereas the flux was in the opposite direction at the Bay sites. Overall, March NO_x fluxes were less than September fluxes and Bay fluxes were greater than Delta fluxes ($P<0.05$). Fluxes in the light were not significantly different than dark fluxes.

Fluxes of NH_4^+ (Fig. 4) were higher in September than in spring ($P<0.05$). Spatially, the fluxes of NH_4^+ generally exhibited the opposite pattern to those of NO_x: although a number of the highest effluxes occurred in the Delta sites with highest influxes at the Bay sites, Bay and Delta environments were not statistically different. Lower flux rates (i.e., high rates of NH_4^+ uptake) were measured under illuminated conditions in both September (Sherman Island I) and March (Franks Tract I, Big Break). Under dark conditions, 8 of the 12 measured sites appeared to be important sources of NH_4^+, with a substantial amount of benthic microalgal attenuation of NH_4^+ effluxes at four of these sites.

Phosphorus Fluxes

Overall trends in SRP fluxes were similar in direction to those of NH_4^+ (Fig. 5). Higher rates were generally observed in March than in September ($P<0.05$), and there was a greater tendency for efflux in the Delta compared to the Bay ($P<0.05$). Overall, dark fluxes were less than light fluxes ($P<0.05$). SRP fluxes under illumination were directed into the sediment, with particularly high (>10 μmol m^{-2} h^{-1}) rates observed in March at Mildred Island, Franks Tract II, Big

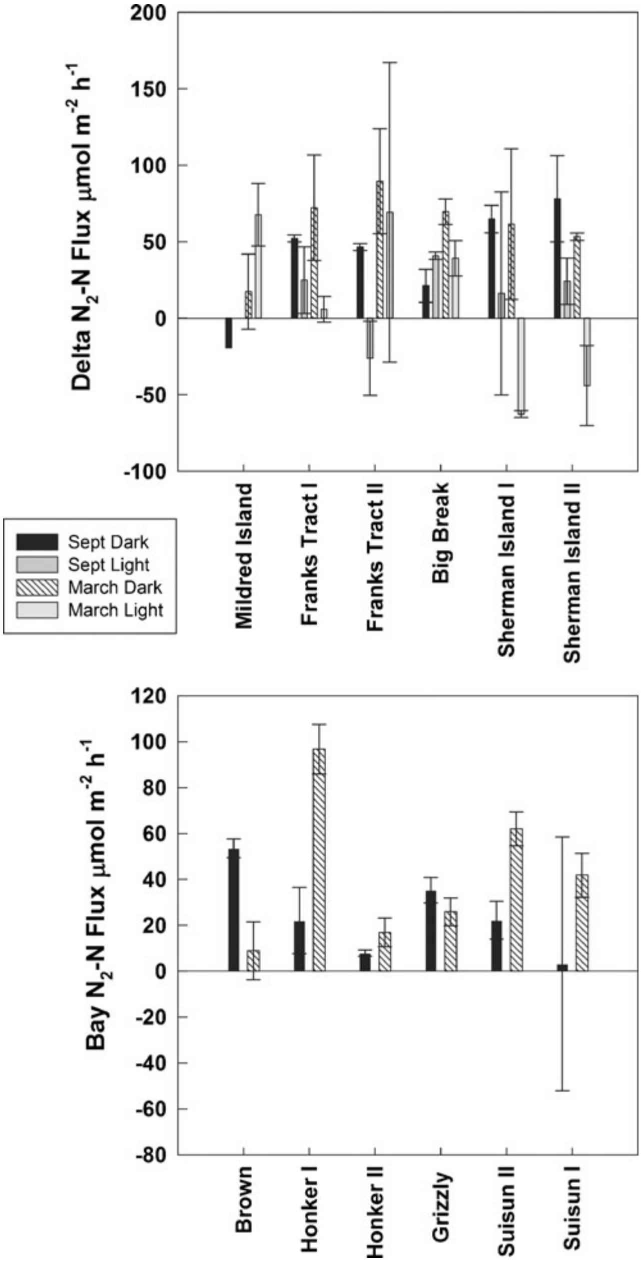

Fig. 2 Sediment–water exchange rates of N_2–N (di-nitrogen). Data include dark fluxes for all sites and light ("illuminated") flux incubations for sites when light reaches the sediment surface. Each *bar* is the mean of duplicate cores, and *error bars* show the data range (except for the March 2012 data at Big Break where $N=6$ and *error bars* are the standard deviation). Negative rates are likely incubation artifacts that are most commonly observed in sediments with benthic microalgal production. Positive rates indicate a flux directed from the sediment to the water column. For the September sampling, Mildred I had no illuminated data

Table 2 ANOVA results for sediment–water exchange and chlorophyll measurements

Flux parameter	Dark fluxes by season (March vs September)	Dark Fluxes By Location (Delta vs Bay)	Delta Only By Illumination (dark vs light)
N_2–N	ns	Bay<Delta	Dk>Lt
NO_x	Mar<Sept	Bay>Delta	ns
NH_4^+	Mar<Sept	–	Dk>Lt
SRP	Mar>Sept	Bay<Delta	Dk>Lt
O_2	Mar<Sept	Bay<Delta	Dk<Lt
Chlorophyll	ns	Bay<Delta	na

Significant differences ($P<0.05$) in fluxes are indicated by < or > symbols, ns is non-significant, and na is non-applicable

Break, and Sherman I and II. Moreover, in March, dark SRP fluxes had a distinct spatial pattern, with moderate to large effluxes in Mildred to Big Break, large rates of uptake in Sherman Island, moderate efflux at Brown, and minimal flux at Honker, Grizzly, and Suisun sites.

Oxygen Fluxes and Sediment Chlorophyll *a*

Fluxes of O_2 in aquatic sediments are the summation of direct uptake of O_2 during anaerobic sediment decomposition, uptake during re-oxidation of reduced species (e.g., sulfides, Fe(II), NH_4^+), and autotrophic O_2 production by benthic microalgae. Dark uptake of O_2 was observed at all sites (Fig. 6). On a seasonal basis, higher O_2 flux rates were observed at all sites during the September sample period compared to March ($P<0.05$). This is consistent with increased sediment metabolic rates as temperature increased to 19–22 °C in September from 12–13 °C in March (Table 1). Large spatial differences were observed, with higher average dark O_2 uptake in Delta sediments than in Bay sediments ($P<0.05$).

Significantly higher rates of benthic photosynthesis ($P<0.05$) were calculated in September (range=393–1,924 μmol $O_2 m^{-2} h^{-1}$; mean, 1,029±628 μmol $O_2 m^{-2} h^{-1}$) than in March (range=144–498 μmol $O_2 m^{-2} h^{-1}$; mean, 115 ±33 μmol $O_2 m^{-2} h^{-1}$). These values should be considered as broad estimates only as cores were exposed to single light levels only, and ambient light levels varied between seasons. The concentrations of sediment chlorophyll *a* were significantly higher ($P<0.05$) in Delta sediments compared to Bay sediments (Fig. 7), but seasonal differences were not significant.

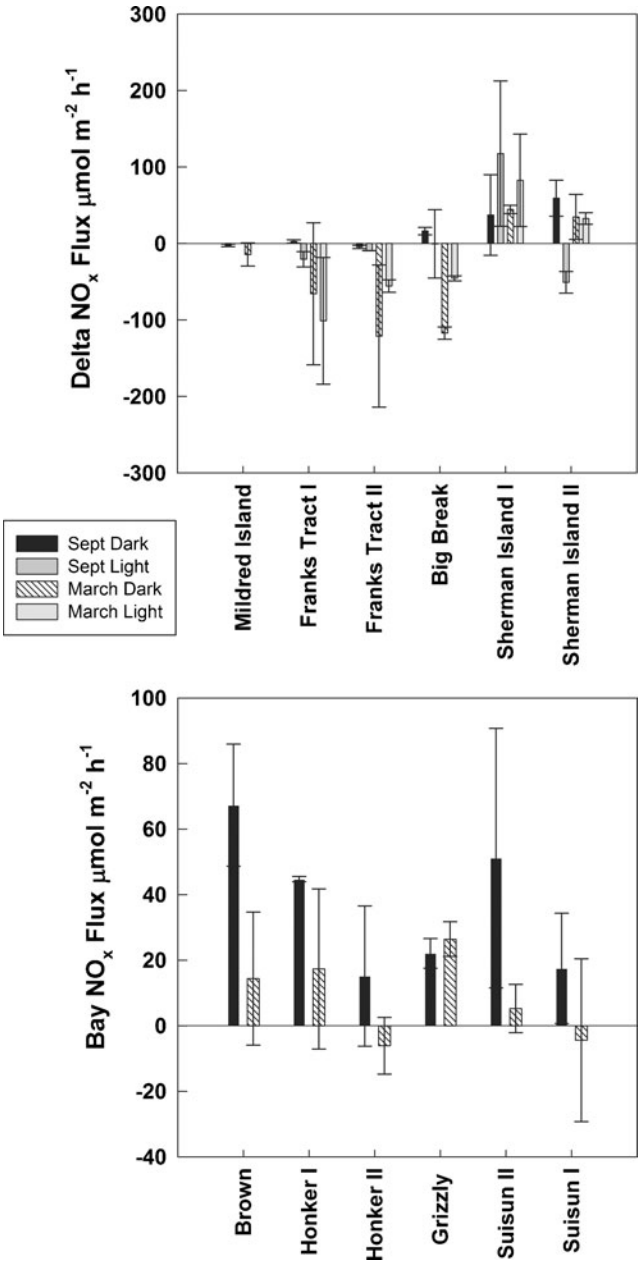

Fig. 3 Sediment–water exchange rates of NO_x^- (i.e., the sum of nitrate and nitrite). Data include dark fluxes for all sites and light ("illuminated") flux incubations for sites when light reaches the sediment surface. Each *bar* is the mean of duplicate cores, and *error bars* show the data range (except for the March 2012 data at Big Break where $N=6$ and *error bars* are the standard deviation). Positive rates indicate a flux directed from the sediment to the water column. For the September sampling, Mildred I had no illuminated data

Discussion

The measurements reported here represent the first seasonal comparison of comprehensive nutrient fluxes from sediments in the San Francisco Bay Delta. Here, we discuss these rates in the context of available data for regionally similar estuaries and for estuaries and coasts worldwide, differential regulation of stoichiometry of the fluxes across the gradient of sites measured, and, finally, the potential contribution of these rates to overall Bay Delta productivity and nutrient loads.

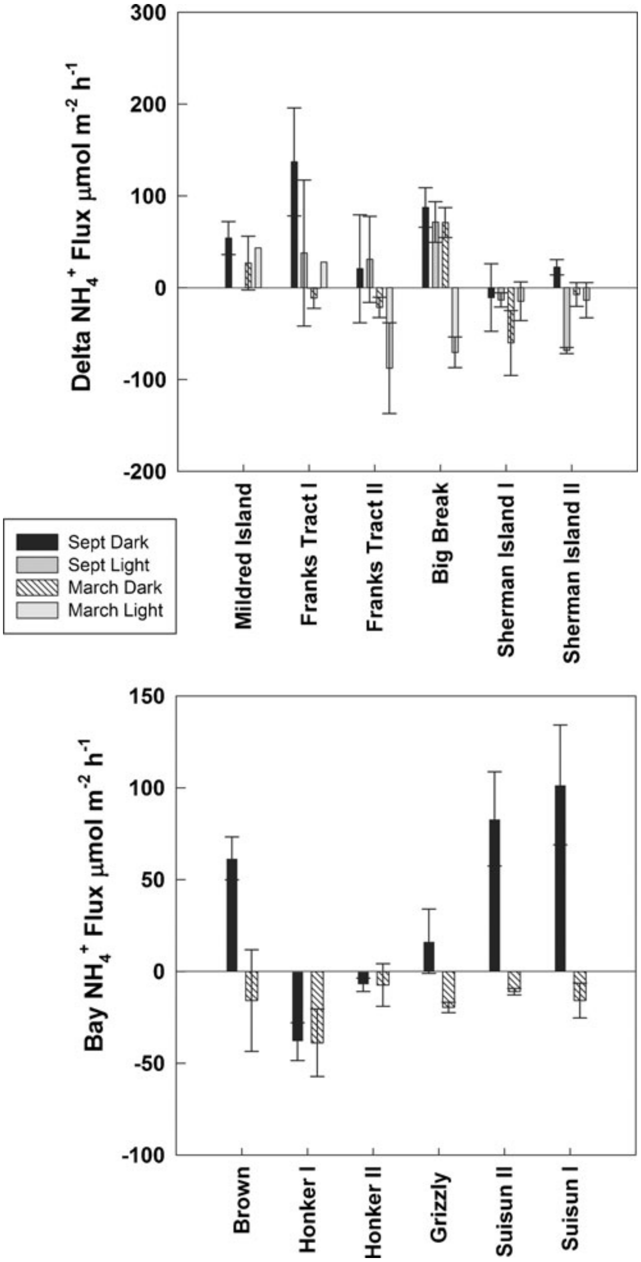

Fig. 4 Sediment–water exchange rates of NH_4^+. Data include dark fluxes for all sites and light ("illuminated") flux incubations for Delta sites when light reaches the sediment surface. Each *bar* is the mean of duplicate cores, and *error bars* show the data range (except for the March 2012 data at Big Break where $N=6$ and error bars are the standard deviation). Positive rates indicate a flux directed from the sediment to the water column. For the September sampling, Mildred I had no illuminated data

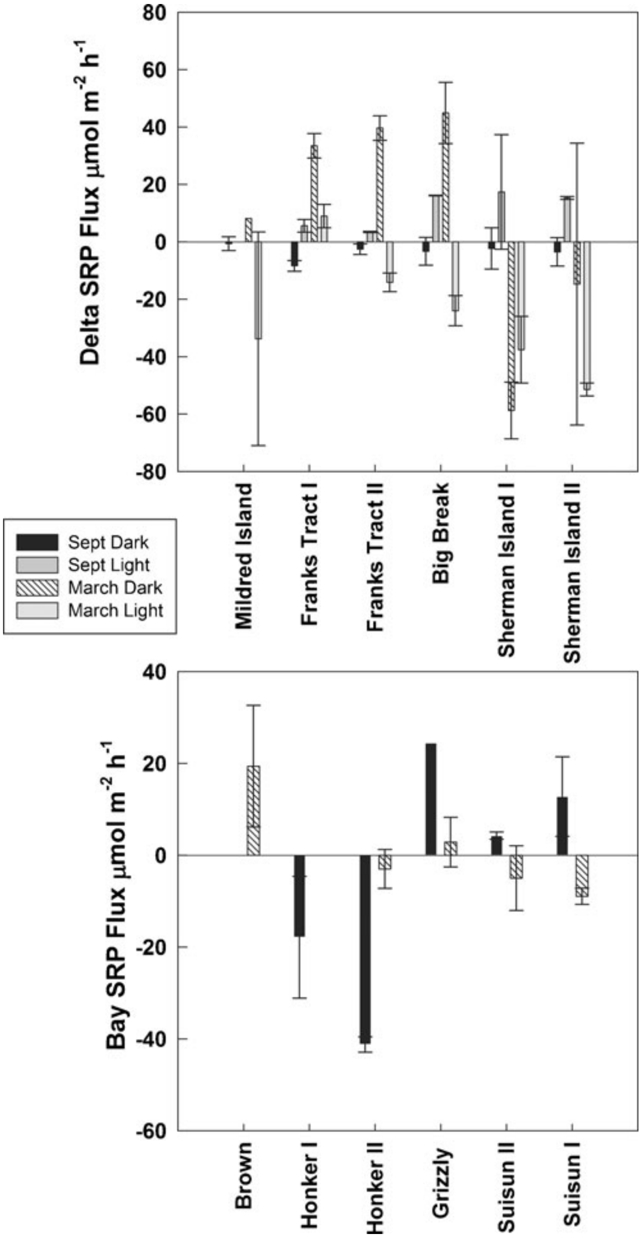

Fig. 5 Sediment–water exchange rates of SRP (soluble reactive phosphorus). Data include dark fluxes for all sites and light ("illuminated") flux incubations for sites when light reaches the sediment surface. Each *bar* is the mean of duplicate cores, and *error bars* are show the data range (except for the March 2012 data at Big Break where $N=6$ and *error bars* are the standard deviation). Positive rates indicate a flux directed from the sediment to the water column. For the September sampling, Mildred I had no illuminated data

Measured Rates in a Regional and Global Context

Fluxes of N were directed both into and out of the sediments and both direction and magnitude varied as a result of the multiple processes contributing to such fluxes, including denitrification, nitrification, assimilation by benthic microalgae, and dissimilatory reduction of NO_3^- to NH_4^+ (DNRA), as well as a broad range of organic matter loading to the different sediments tested. When compared to previous measured rates of denitrification worldwide compiled by Joye and Anderson (2008) using similar MIMS techniques, the rates measured herein are comparable to most other estuaries (Table 3). Uptake rates of NO_x in the upper Delta are much higher than observed in other northern California sites such as Tomales Bay, but similar rates have previously been reported in the NO_x-enriched Elkhorn Slough (Dollar et al. 1991; Caffrey et al. 2002). The NH_4^+

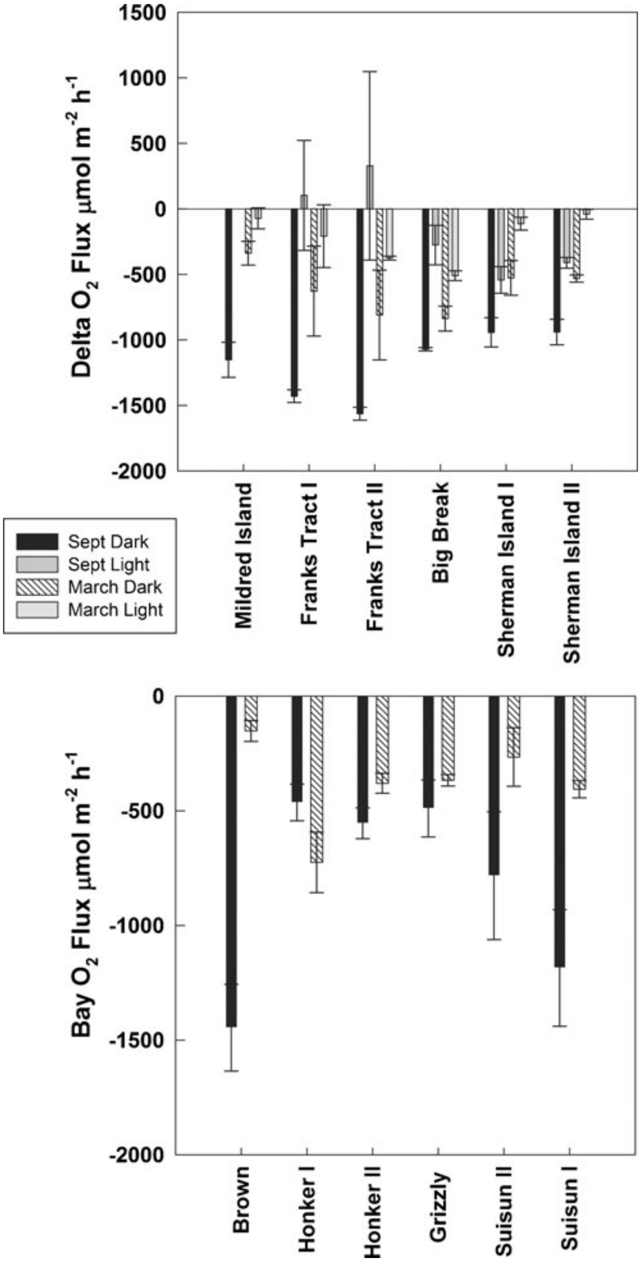

Fig. 6 Sediment–water exchange rates of oxygen for Delta (*top panel*) and Bay (*bottom panel*) environments. Data include dark fluxes for all sites and light ("illuminated") flux incubations for Delta sites where light reaches the sediment surface. Each *bar* is the mean of duplicate cores, and *error bars* show the data range (except for the March 2012 data at Big Break where N=6 and error bars are the standard deviation). Positive rates indicate a flux directed from the sediment to the water column. For the September sampling, Mildred I had no illuminated data

effluxes in the Delta–Bay transect had most effluxes <100 µmol m^{-2} h^{-1}, with many sites showing uptake in the light and occasionally in the dark. In the Bay Delta region, Caffrey (1995) reported net NH_4^+ production rates at Rio Vista and Suisun Bay that were <100 µmol m^{-2} h^{-1} at all seasons. However, regionally, NH_4^+ flux rates measured in Tomales Bay and Elkhorn Slough were somewhat higher than our observations (Dollar et al. 1991; Caffrey et al. 2002, 2010). Boynton and Kemp (2008) also compiled a comparative data set of dark NH_4^+ effluxes for many estuaries, and these values also showed most effluxes <100 µmol m^{-2} h^{-1}.

Similar to previously reported data for Elkhorn Slough and Tomales Bay (Caffrey et al. 2002), the SRP fluxes in the Bay–Delta transect had large rates of efflux and influx. The only previously available study on benthic fluxes nutrients in the upper Bay Delta in late summer reported P efflux rates that ranged from insignificant to ~0.06 mmol m^2 day^{-1}, considerably lower than rates previously found for the more saline reaches of the estuary and considerably lower than those of NH_4^+ (Kuwabara et al. 2009). The SRP efflux rates reported herein are significantly higher than those of Kuwabara et al. (2009), but different methodologies were applied in these two studies. In Tomales Bay, California, USA, Chambers et al. (1995) estimated that release of particle-bound P was ~12 % of the benthic flux of P in sediments that were sulfide-rich. In their global comparison, Boynton and Kemp (2008) showed that roughly one in ten dark SRP flux measurements had a net uptake of SRP into the sediment, indicating that SRP uptake is not uncommon in estuarine sediments. In fact, of the 228 studies they summarized in which SRP fluxes were measured for sediments <5 m depth, the SRP fluxes for the Bay Delta were in the upper range, if not exceeding these previous studies. In the Bay Delta, where P was previously measured in the upper few centimeters of sediment, concentrations were 5–10 µmol g^{-1} in the confluence region, but significantly higher at freshwater sites (Nilsen and Delaney 2005). It has been suggested that localized regions of high benthic productivity may result in elevated pH which, in turn, may result in a change in SRP fluxes, from influx to efflux (Glibert et al. 2011; Gao et al. 2012). That higher efflux of SRP was observed in all Bay Delta sites would be consistent with this hypothesis.

Coastal and estuarine sediments with benthic microalgae have a broad range of chlorophyll *a* concentrations, ranging up to 560 mg m^{-2} (MacIntyre et al. 1996); the highest chlorophyll *a* concentrations measured in this study were found in September at Franks Tract I (replicate cores with 66 and 91 mg m^{-2}; Fig. 7). The sediment chlorophyll *a* data reported here compared favorably, on average, with those previously reported by Kuwabara et al. (2009), but there were spatial differences. As an example, at Sherman Island, the data reported here are much higher than Kuwabara et al.'s (2009) observations that showed no detectable chlorophyll *a*; based on single analyses from four cores during each season, the average observed during this study was 14±3 and 10±4 mg m^{-2} chlorophyll *a* in September and March. Dark sediment O_2 fluxes were <2000 µmol m^{-2} h^{-1}, a number consistent with estuarine observations worldwide (Boynton and Kemp 2008). The highest rate of O_2 uptake are similar to

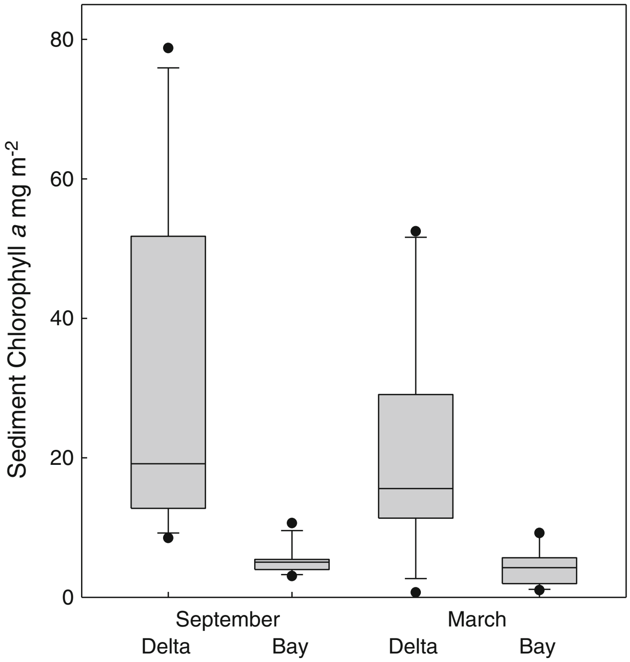

Fig. 7 Sediment chlorophyll *a* concentrations from Delta and Bay environments in September 2011 and March 2012. The *box plots* show the median as the line within the box, the box represents the 25–75th percentiles, and the *error bars* are the 0–25 and 75–100 percentiles. A Kruskal–Wallis one-way analysis of variance on ranks showed that the Delta and Bay locations were significantly different ($P<0.01$) and that there were no temporal differences

those in nearby Tomales Bay (Dollar et al. 1991), with the Tomales Bay annual average O_2 uptake similar to the March 2012 rates reported herein.

Elemental Stoichiometry of Fluxes

The rates of ΣN flux ($\Sigma N=NH_4^{+}+NO_x^{-}+N_2$–N flux) can be compared to sediment O_2 demand to examine the stoichiometric relationship of N flux to organic matter decomposition. Implicit in this analysis is that (1) organic matter sources have a reasonably similar composition, with Redfield algal organic matter used as a key metric, (2) microbial processes yield remineralized N and P in expected ratios, and (3) O_2 fluxes are a suitable measure of metabolism. Sediment O_2 demand has the opposite sign of O_2 fluxes and while an imperfect measure of metabolism (Banta et al. 1994), provides a useful comparison to nutrient fluxes.

In September, ΣN fluxes generally increased with increasing sediment O_2 demand, with the greatest scatter in the light fluxes from Delta sediments (Fig. 8). In March, the agreement with stoichiometry was much weaker, with illuminated Delta sediments showing a ΣN deficit while dark Delta sediments showed a N excess. The balance of N on a diel cycle may better reflect the true net balance of these Delta sites. In March, the bay sediments appeared to follow stoichiometry much more closely. The September flux of SRP relative to O_2 demand generally showed that dark incubations tended to have a SRP deficit, while illuminated sediments had SRP fluxes slightly in excess of stoichiometry. In March, illuminated sediment showed a SRP deficit relative to O_2 uptake, suggesting excess SRP uptake beyond nutritional requirements.

Overall, the lack of tight relationships between observed and expected C/N/P suggests that controls beyond the rates of organic matter remineralization are important. Nitrification and denitrification change dissolved inorganic N effluxes, but conserved stoichiometry is not observed, even when N_2–N fluxes are considered. Such conservation of ratios would not necessarily be expected (Glibert et al. 2011). Benthic microalgae can skew elemental ratios by "luxury" uptake during periods without light and by intercepting remineralized N and P. Stoichiometric relationships for SRP are affected by

Table 3 Compilation of rates of denitrification measured in estuaries and coastal regions worldwide

Estuary or coastal region	Denitrification rate (mmol m^{-2} day^{-1})	Reference
		Kana et al. (1998)
Laguna Madre, TX	0.48	An et al. (2001)
	0.2–0.98	An and Gardner (2002)
Mid-Atlantic Bight	1.74	Laursen and Seitzinger (2002)
Chesapeake Bay	5.4–12	Newell et al. (2002)
Baffin Bay, TX	0.4–1.63	An and Gardner (2002)
Lagoons, Sydney, AU	0.19–1.66	Eyre and Ferguson (2002)
Readings Bay, New Brunswick, AU	1.2–7.2	Webb and Eyre (2004)
Bremer River, AU	3.78	Cook et al. (2004b)
Huon Estuary, AU	0.01–0.12	Cook et al. (2004a)
Brunswick Estuary, AU	0.38-5.95	Ferguson et al. (2004)
	0.07–1.4	Eyre and Ferguson (2005)
Neuse River Estuary, NC	0–6.62	Fear et al. (2005)
Matagorda Bay, TX	0.54+0.1	Gardner et al. (2006)
Nueces Estuary, TX	0.96±0.2	Gardner et al. (2006)
Sapelo Island, GA	0.1–0.2	Porubsky et al. (2009)
Dover Bluff, GA	0–0.4	Porubsky et al. (2009)
Okatee Estuary, SC	0–0.2	Porubsky et al. (2009)
Randers Fjord, DK	5.2–8.0	Risgaard-Petersen et al. (2004)
Norsminde Fjord, DK	4.6–5.7	Risgaard-Petersen et al. (2004)
Delta sites	0.7–0.9	This study
Bay sites	0.6–1.0	This study

All rates reported here were determined using MIMS methodology. This compilation is a subset of all denitrification rates reported by Joye and Anderson (2008). For our Delta sites, we used day length to determine a daily denitrification rate from our light and dark incubations, the range represents the data from the two sample times

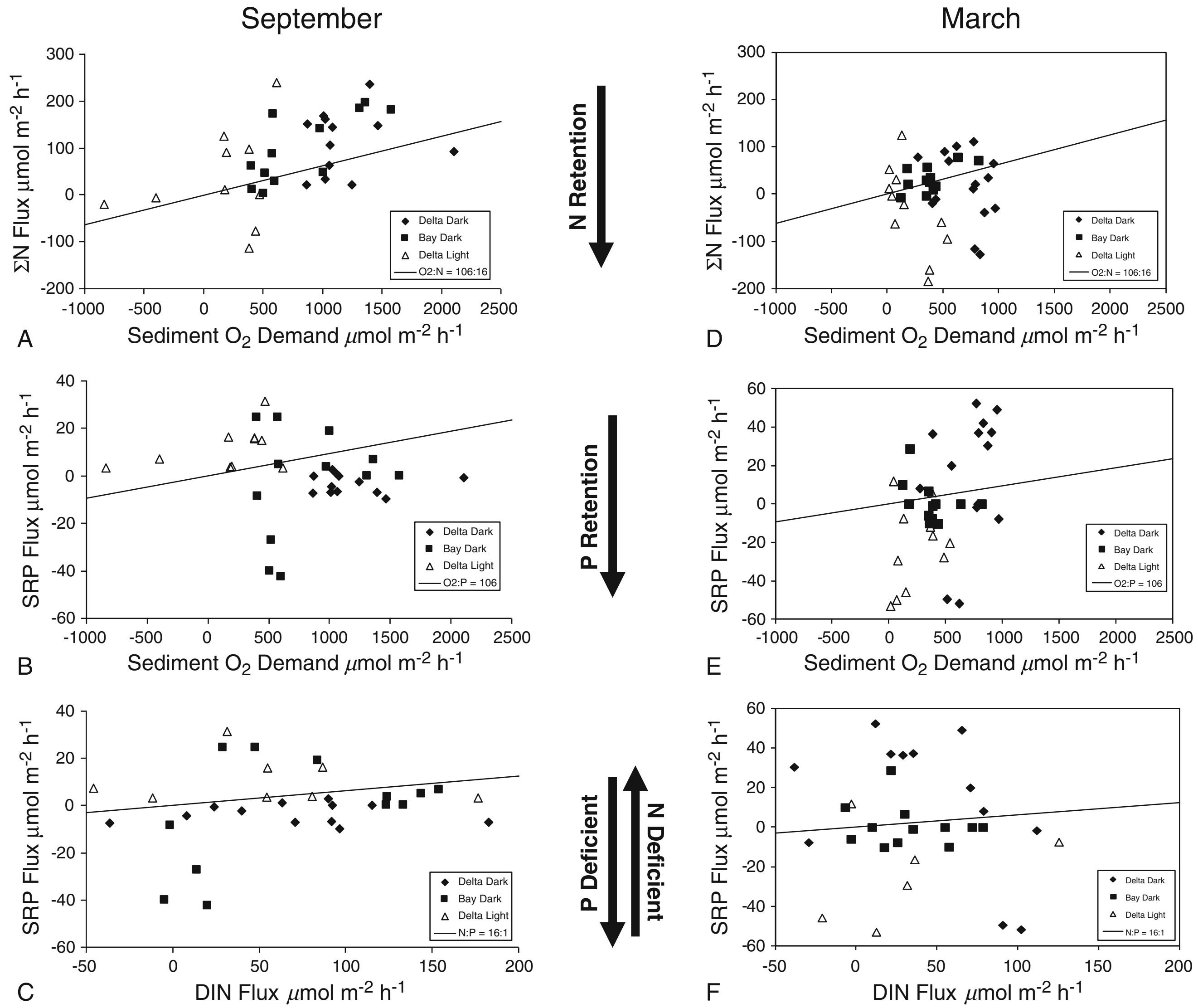

Fig. 8 *A–C* September 2011 property plots of sediment–water exchange; sediment oxygen demand has the opposite sign of oxygen fluxes, with negative values for net photosynthetic fluxes. Data include bay stations and both light and dark incubations of Delta sediments. *A* shows a plot of sediment oxygen demand versus ΣN flux (N_2–N+NH_4^++NO_x) showing general agreement, with N efflux in excess of the Redfield ratio. The SRP fluxes below the Redfield line in *B* indicate a net retention of organic P within the sediments. The SRP versus DIN plot (***C***) indicates that SRP is generally lower than predicted by stoichiometry, suggesting that during sediment nutrient recycling that N is generally in excess of P. *D–F*: As for *A–C* except for March 2012

SRP retention/release on the surface of iron oxide minerals; the predominance of inorganic forms of P in these sediments (Nilsen and Delaney 2005) can result in (1) P retention and (2) possible release under low redox conditions (Lehtoranta et al. 2009), changes in salinity (Froelich 1988; Gardolinski et al. 2004), and changes in pH (Glibert et al. 2011; Gao et al. 2012).

The salinity gradient encompassed in this study did not show consistent large differences in sediment N or P biogeochemistry, although stoichiometric changes along the salinity gradient were expected and observed. Three Bay sites had significant P retention relative to DIN, while all the Delta sites from the light experiments had excess P release relative to N. Large differences along the spatial (salinity) gradient were also observed in the form of N flux, i.e., the ratio of NO_x/NH_4^+. Salinity generally has an opposite effect on N fluxes compared to P fluxes. Whereas P flux rates are often higher in saltwater, rates of NH_4^+ flux are higher in freshwater (Jordan et al. 2008 and references therein), and this can accentuate the discrepancy between N/P ratios along the salinity gradient, and indeed the patterns herein are consistent with this generally expected pattern. Consistent with this idea, comparisons of the NH_4^+/PO_4^{3-} ratio along the salinity gradient of four sub-estuaries of Chesapeake Bay (Patuxent, Potomac, Choptank, and Bush Rivers) also revealed in common a switch from molar ratios >16 to <16 as salinity increased,

Table 4 Summary of total net N input for the length of Sacramento (SAC) and San Joaquin Rivers (SJR) indicated

	Total area (km^{-2})	River TN yield (kg N km^{-2} year^{-1})	Daily TN yield (kg N km^{-2} day^{-1})	Total daily net TN yield (kg N day^{-1})	Total daily net N yield (tonnes N day^{-1})
SAC	61,721	126	0.35	21,602	21
SJR	19,030	135	0.36	6,851	6.8

All data are based on values from the early 2000s, as reported by Sobota et al. (2009)

with a major breakpoint in the salinity range of 1–4 (Hartzell et al. 2010). Seitzinger et al. (1991b) suggested that lower denitrification efficiencies in saltwater compared to freshwater arise, at least in part, due to decreased adsorption of NH$_4^+$ at higher ionic strengths which leads to poor efficiency of nitrification.

Potential Delta Impact

Estimated benthic microalgal productivity was surprisingly high in Delta sediments, with a large range in both biomass and productivity. The median rates of O$_2$-based photosynthesis estimated here were 795 and 395 μmol O$_2$m^{-2} h^{-1} for September and March, respectively; these data are equivalent to 119 and 57 mg C m^{-2} day^{-1} for the day length at each sample period. While these rates are estimates and more detailed measurements as a function of irradiance are required, these rates are similar to benthic microalgal photosynthetic rates observed in a wide range of coastal environments (MacIntyre et al. 1996). Guarini et al. (2002) examined potential productivity in San Francisco Bay tidal environments using resuspended benthic algae and a modeling extrapolation, concluding that spatial variation in benthic productivity would be large, but measured no in situ or ex situ benthic microalgal production.

Jassby et al. (2002) modeled phytoplankton production in the River Delta with a predicted annual range of 24–131 g C m^{-2} year^{-1}, equivalent to 66–359 mg C m^{-2} day^{-1}, based on water column estimated rates only. Kimmerer et al. (2012) suggested phytoplankton photosynthetic rates were at the lower end of Jassby et al.'s range. Jassby et al. (2002) calculated an average water column chlorophyll *a* concentration of ~5 mg m^{-3}; to obtain the equivalent median areal concentration of sediment chlorophyll *a* at the Delta sites measured here, a ~4 m water column would be required. Given that the Bay Delta has long been considered a system of exceptionally low phytoplankton productivity (Jassby et al. 2002; Kimmerer et al. 2012), the potentially high contribution of benthic productivity could significantly alter that perspective. Depending on depth, or the proportion of Delta sediment that has sufficient light to support benthic microalgal photosynthesis, benthic microalgae could represent an important proportion of photosynthesis in the Delta. However, further measurements of benthic chlorophyll *a*, photosynthesis, and benthic microalgal effects on nutrient flux (e.g., Sundback et al. 2000; MacIntyre et al. 2004) are necessary to better constrain the relative importance of benthic microalgae, particularly using controlled light incubations. The role of variable depth and light attenuation in such macrotidal environments require modeling efforts to best predict productivity. The lack of detailed hypsography necessarily limits the strength of these conclusions, but inclusion of microalgae in system productivity estimates may be important.

A difference in the eastern delta and the more saline bays is the presence/absence of benthic microalgae, with system hypsography and light penetration being major controls on benthic algal biomass. Regardless of salinity, the supply of labile organic matter to sediment is also a key determinant of sediment N fluxes. As in other shallow ecosystems, benthic microalgae exert a large influence on nutrient flux dynamics (Tyler et al. 2003). Moreover, the potential nutritional benefits of benthic microalgae to higher trophic levels (Middelburg et al. 2000) may be important to the Bay Delta ecosystem trophic dynamics.

The release of sediment DIN (the sum of NH$_4^+$+NO$_3^-$) represent a potentially important N input to the water column that can support water column primary production (Fisher et al. 1982). The average rates of DIN release in Delta and Bay environments were 1.1 and 1.7 mmol m^{-2} day^{-1} in September; using Redfield stoichiometry for C/N, this could support algal productivity of 87 and 135 mg C m^{-2} day^{-1}, respectively. Thus, in September, such remineralization provides an amount of N roughly equivalent to the nutritional needs of the phytoplankton community. In March, there was a

Table 5 Summary of total net P input for the length of Sacramento (SAC) and San Joaquin Rivers (SJR) indicated

	Total area (km^{-2})	River TP yield (kg P km^{-2} year^{-1})	Daily TP yield (kg P km^{-2} day^{-1})	Total daily net TP yield (kg P day^{-1})	Total daily net P yield (tonnes P day^{-1})
SAC	61,721	21	0.057	3,518	3.5
SJR	19,030	14	0.038	723	0.7

All data are based on values from the early 2000s, as reported by Sobota et al. (2011)

net uptake of DIN balanced by N_2–N flux that results in a potential loss of N to the phytoplankton community.

The role of Delta sediments in the nutrient balance in this ecosystem can be compared to nutrient loading rates for the Bay Delta ecosystem, recognizing that any extrapolations at the current time are constrained because of indeterminate areas of photosynthetic sediments. We view these calculations as providing preliminary information on the relative scales of these processes. The daily average N_2–N flux rate calculated over 24 h of light/dark conditions from this study ranged from 0.7 to 0.9 mmol m^{-2} day^{-1}; when extrapolated to the whole Delta area of 2.3 10^8 m^2 (Jassby et al. 2002), 2.2–2.9 t N day^{-1} would be removed via this process. For comparison, recognizing that such estimates at the current time are approximate, the ~2.5 t N removed via denitrification is roughly one sixth of the ~15 t N day^{-1} of the wastewater load from the Sacramento Regional Wastewater Facility on the Sacramento River (Glibert et al. 2011). Using the integrative estimates from the Lower Sacramento and San Joaquin Rivers provided by Sobota et al. (2009; Table 4), denitrification would represent one tenth of the total daily net N yield of these two rivers. Using the benthic microalgal requirement for N based on Redfield stoichiometry, a maximum uptake estimate of 2–5 t N day^{-1} within this community is calculated. Depending on the area of benthic photosynthetic uptake, this suggests that an amount up to ~20 % of the inputs could either be removed via denitrification or taken up by benthic microalgal photosynthesis.

The benthic microalgal requirement for P would be equivalent to 0.3–0.7 t P day^{-1}, with wastewater loading rates from the Sacramento Wastewater Treatment Facility of 1–2 t P day^{-1} (Glibert et al. 2011). Similarly, using the integrative estimates of total P yields for these rivers provided by Sobota et al. (2011; Table 5), the removal of P due to benthic uptake would be in the range of 10-100 %. Although such budgetary estimates are approximate, they suggest a greater potential for N relative to P to be exported downstream where it may support phytoplankton production displaced spatially from the upstream sources.

In summary, rates of sediment nutrient fluxes were shown to be significant and dynamic, with regional variability from the freshwater delta to the more saline Suisun Bay. Rates of the processes measured here fell largely within the broad range of rates for such processes reported worldwide. While rates of N and P fluxes had been hypothesized to be higher in the late summer than spring, due to the contribution of increased microalgae during late summer, many of the fluxes were, in fact, higher in spring than summer. Extrapolating from both chlorophyll *a* and O_2 fluxes, the sediments may potentially have large impacts on estimates of total system productivity. While these data have provided the first such estimates of nutrient fluxes for this region of the Bay Delta, these rates are nevertheless limited in scope. They represent only two seasons and only the more shallow sites of the Bay Delta. There is much more to be understood regarding the controls on these rates, their regional and seasonal variability, and how such rates may be impacted by biotic changes, such as those of the invasive clam, *Potamocorbula*.

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

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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, $<4\ \mu mol\ L^{-1}$ 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 $4\ \mu mol\ L^{-1}$ 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

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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 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

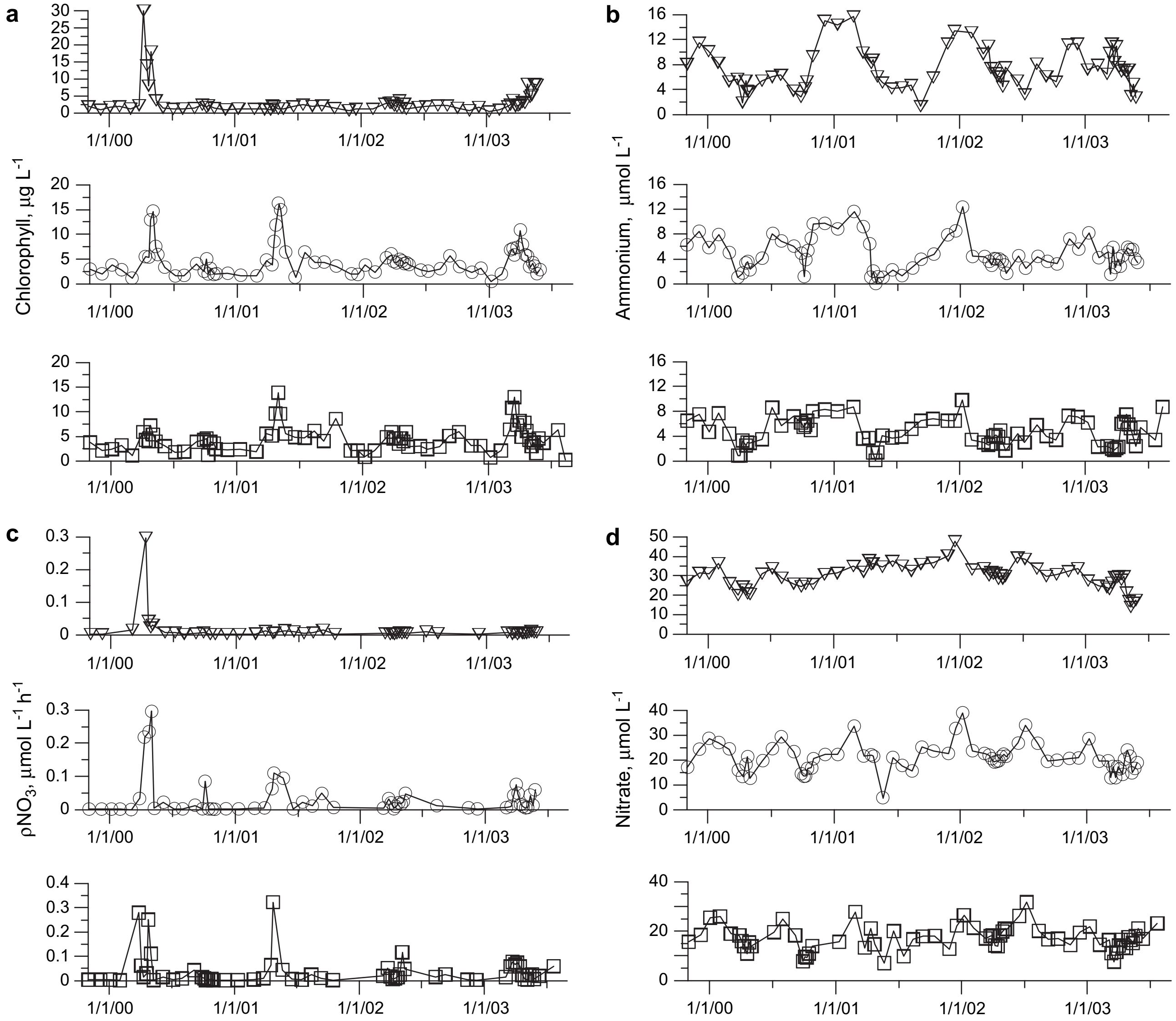


Fig. 1. Surface time series data collected in Suisun (triangles), San Pablo (circles) and Central Bays (squares) from November 1999 to August 2003. (a) Chlorophyll *a*, $\mu g\,L^{-1}$, (b) NH_4, $\mu mol\,L^{-1}$, (c) trace $\rho^{15}NO_3$, $\mu mol\,L^{-1}\,h^{-1}$, (d) NO_3, $\mu mol\,L^{-1}$.

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 $\mu mol\,L^{-1}$ NH_4 increasing rapidly by 1 $\mu mol\,L^{-1}$ 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 $>20\,\mu mol\,L^{-1}$ (Fig. 1d), NH_4 concentrations $>10\,\mu mol\,L^{-1}$ and low specific N uptake rates, VNH_4 and VNO_3, $<0.005\,h^{-1}$ (Fig. 5a). Chlorophyll was also low, $<2\,\mu g\,L^{-1}$ as were ρNH_4 and ρNO_3, $<0.02\,\mu mol\,L^{-1}\,h^{-1}$ (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. $<2\,\mu mol\,L^{-1}$, 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 $\mu mol\,L^{-1}$ (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

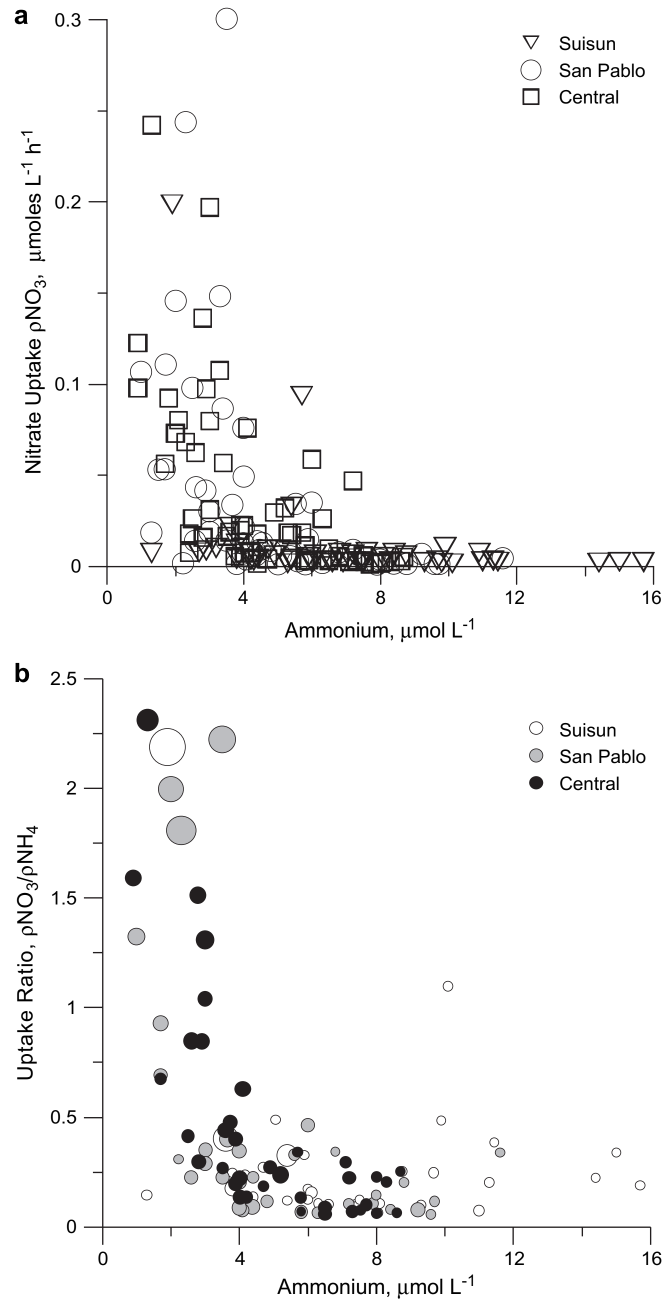


Fig. 2. (a) Saturated ρNO_3, μmol L^{-1} h^{-1} versus NH_4, μmol L^{-1} for Suisun, San Pablo and Central Bays and (b) ratio of saturated ρNO_3 to ρNH_4 versus NH_4, μmol L^{-1}. The points in the graph are shown as bubbles that indicate chlorophyll concentration.

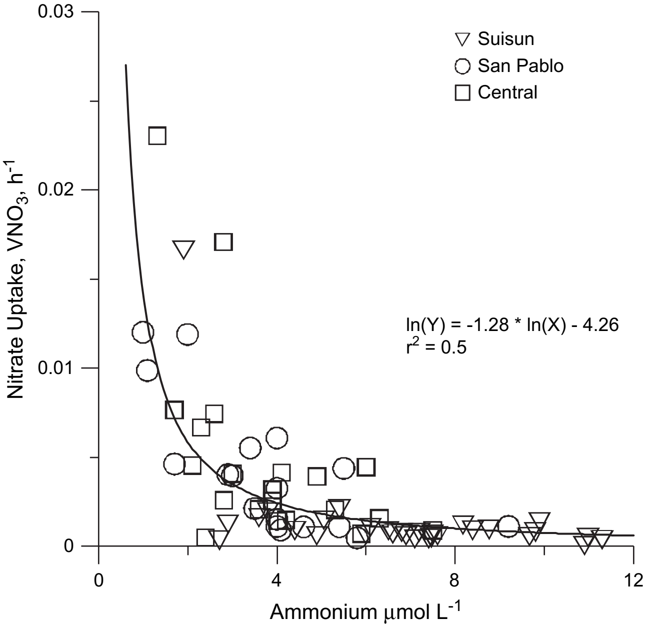


Fig. 3. Trace VNO_3, h^{-1} versus NH_4 concentration, μmol L^{-1} for the spring bloom periods in Suisun, San Pablo and Central Bays. Exponential line fit through the San Pablo and Central Bay data.

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 μmol L^{-1} value when chlorophyll accumulation based on NH_4 uptake begins, and the second, about 1 μmol 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 μmol 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

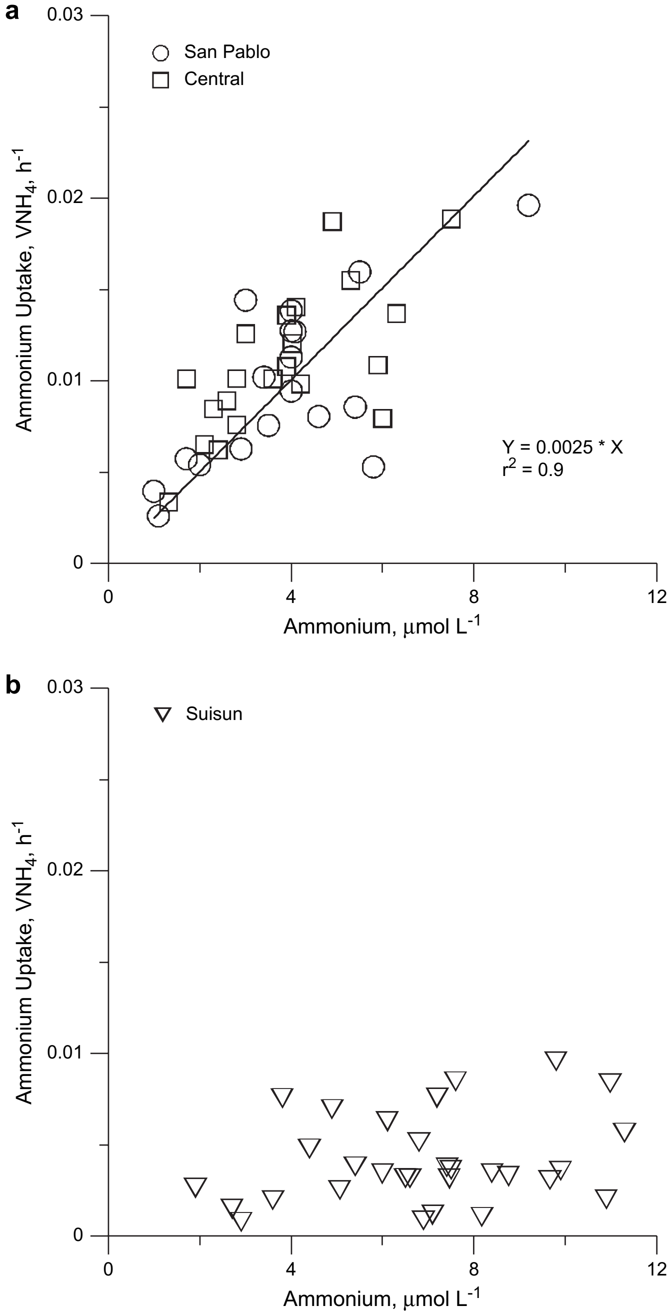


Fig. 4. Trace VNH_4, h^{-1} versus NH_4 concentration, $\mu mol\,L^{-1}$ for the spring bloom periods in (a) San Pablo and Central Bays, (b) Suisun Bay.

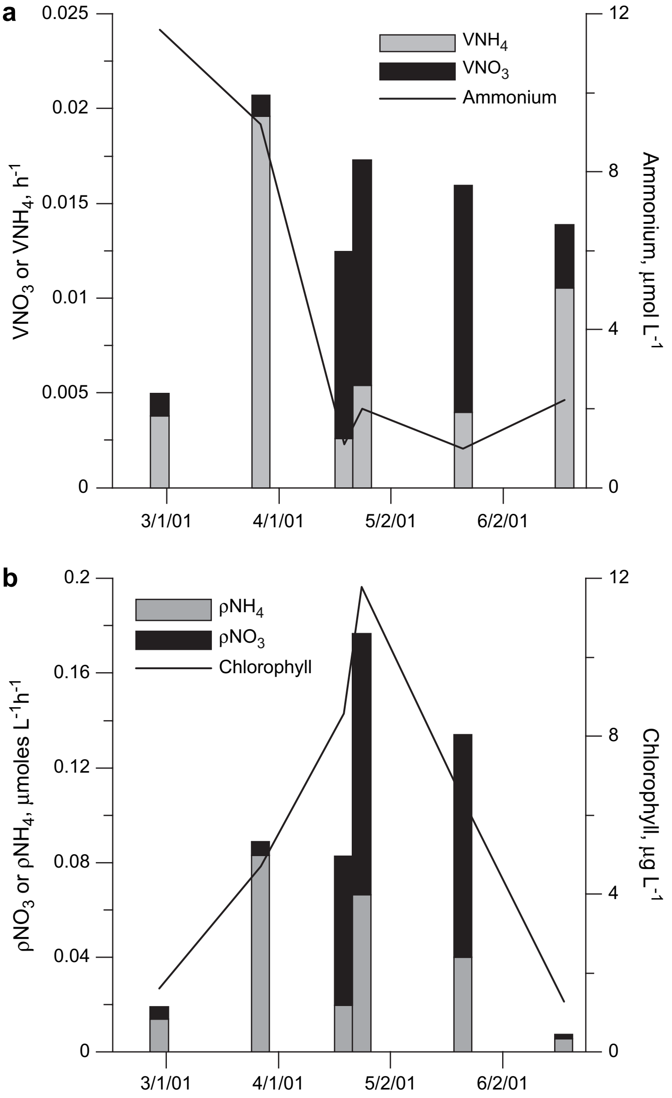


Fig. 5. (a) Trace VNH_4, h^{-1}, trace VNO_3, h^{-1} and NH_4, $\mu mol\,L^{-1}$, (b) trace ρNH_4, $\mu mol\,L^{-1}\,h^{-1}$, trace ρNO_3, $\mu mol\,L^{-1}\,h^{-1}$ and chlorophyll concentration, $\mu g\,L^{-1}$ for San Pablo Bay in spring, 2001. NO_3 concentration at start was 33.6 $\mu mol\,L^{-1}$.

on a daily basis and without the light limitation that results from turbulent mixing in situ. Changes in uptake of NH_4 and NO_3 in response to different ambient 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 NH_4 (low ambient NH_4 <5 $\mu mol\,L^{-1}$ and higher, >5 $\mu mol\,L^{-1}$) showed depletion of NO_3 to occur once NH_4 had been reduced to low levels (Fig. 7a,b). Depletion of NO_3 began after 1 day in the enclosures with low initial NH_4 (enclosures A, B; Fig. 7a). In the enclosures (C, D, E, F) with higher initial ambient levels of NH_4, there was a lag before NO_3 was drawn down and NO_3 concentrations in the enclosures decreased (Fig. 7b). Maximum VNO_3 was delayed (Fig. 7c) in most of the enclosures with higher initial NH_4 (enclosures C, E, F). Maximum specific NO_3 uptake was reached after 2–3 days (Fig. 7c) depending on the initial concentration of NH_4, with values of VNO_3 exceeding those of VNH_4. There was no change in VNH_4 uptake with time in the enclosures (Fig. 7d). Chlorophyll *a* biomass accumulated in all enclosures reaching almost 30 $\mu g\,L^{-1}$ (Fig. 7e) supported primarily by 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 NH_4 to enclosures to see if NO_3 uptake was suppressed was investigated in spring 2003 using 20-L enclosures filled with Central Bay water and different experimental additions of NH_4 (5 to 30 $\mu mol\,L^{-1}$). Increased NH_4 concentration resulted in a delay of the onset of NO_3 uptake, or increased lag time before NO_3 depletion was observed

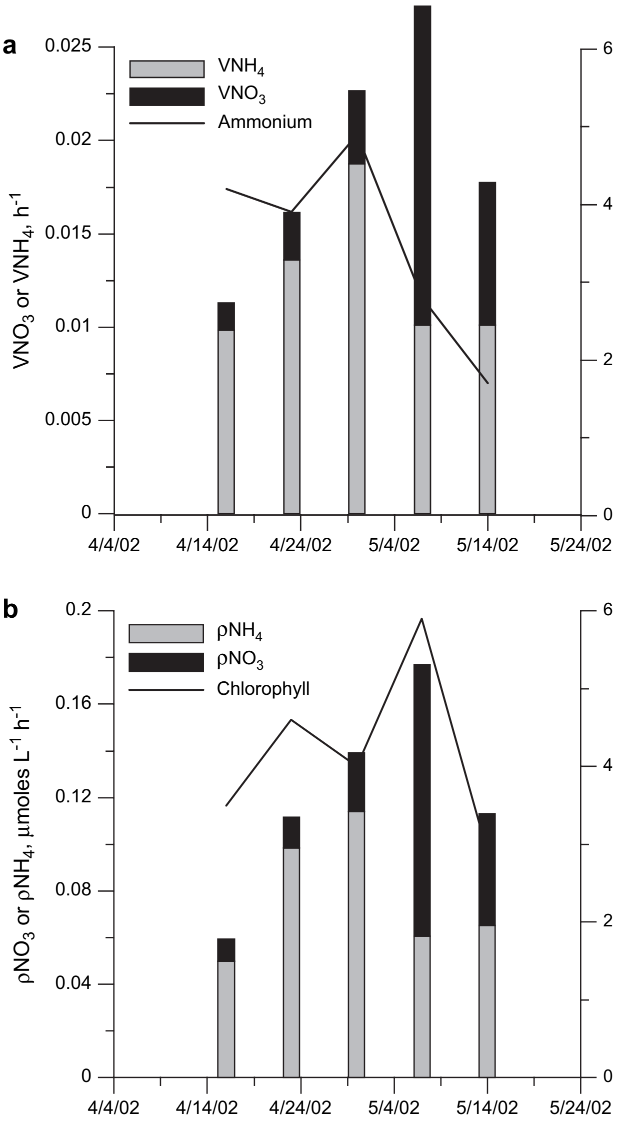


Fig. 6. (a) Trace VNH_4, h^{-1}, trace VNO_3, h^{-1} and NH_4, µmol L^{-1}, (b) trace ρNH_4, µmol L^{-1} h^{-1}, trace ρNO_3, µmol L^{-1} h^{-1} and chlorophyll concentration, µg L^{-1} for Central Bay in spring, 2002. NO_3 concentration at start was 14 µmol L^{-1}.

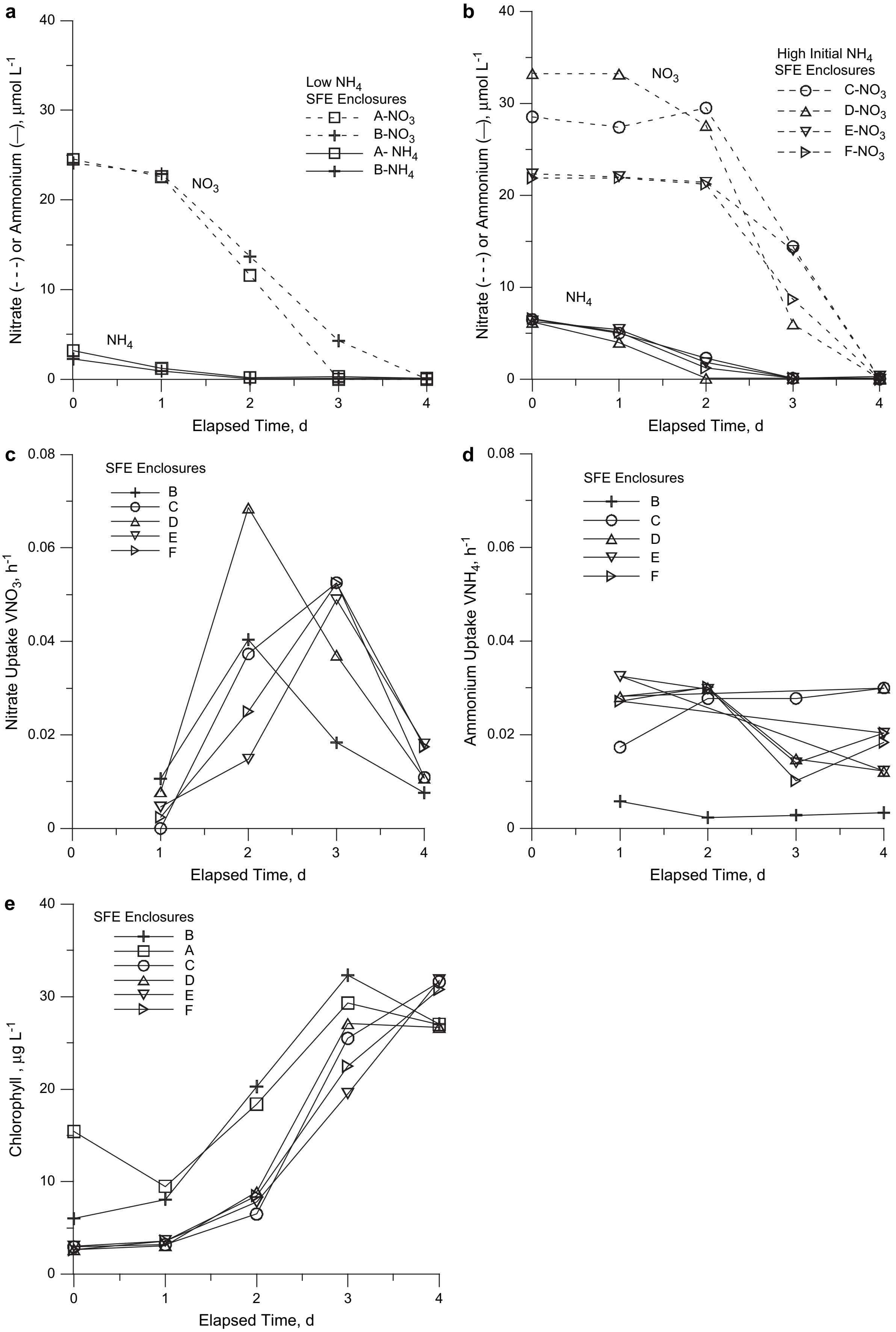
(Fig. 8a). The enclosure with no experimental addition had an initial NH_4 concentration of 5.7 µmol L^{-1} and required 2 days to reduce the NH_4 concentration to a low value (0.8 µmol L^{-1}; Fig. 8b), at which point NO_3 decreased in the enclosure (Fig. 8a). At the highest addition, 30 µmol L^{-1}, no NO_3 decrease was observed during the 4 days of the experiment. When the values of VNO_3 from the different sets of additions were combined for all 4 days of the experiment and plotted versus the NH_4 concentration at the sampling time of the uptake measurement (Fig. 8c), high values of VNO_3 appear only at low NH_4 concentrations, ca. 1 µmol L^{-1}. At higher NH_4 concentrations VNO_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 VNO_3 to VNH_4 (Fig. 8d), at low NH_4 concentrations shows the same pattern as seen for the uptake ratio in the three bays (Fig. 2b). These results demonstrate that the NH_4 inhibition effects apparent in the bay can be experimentally reproduced by the addition of NH_4 to SFB water, i.e. a direct demonstration of NH_4 inhibition of 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 NO_3 concentrations in the estuary are generally unavailable to the phytoplankton due to the presence of 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 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 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 NH_4 uptake (Fig. 5b). If the combination of these processes results in NH_4 concentrations being reduced to below 4 µmol L^{-1} to a value of about 1 µmol L^{-1} (Fig. 3), 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 NH_4 and the higher ambient concentration of NO_3. Mass balance considerations indicate that to obtain the concentrations of chlorophyll measured in SFB, ambient NH_4 is insufficient and NO_3 must be used also. If NO_3 uptake is not turned on, the biomass increase is small and limited to the amount of NH_4 taken up. In years with insufficient dilution, and higher levels of NH_4 (i.e. >4 µmol 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 NH_4 and regeneration of the bloom-produced organic nitrogen by grazing or by bacterial action at the sediment surface (Caffrey, 1995) results in NH_4 concentrations returning to levels inhibiting 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
0
1
2
3
4
0
10
20
30
40
0
0.02
0.04
0.06
0.08

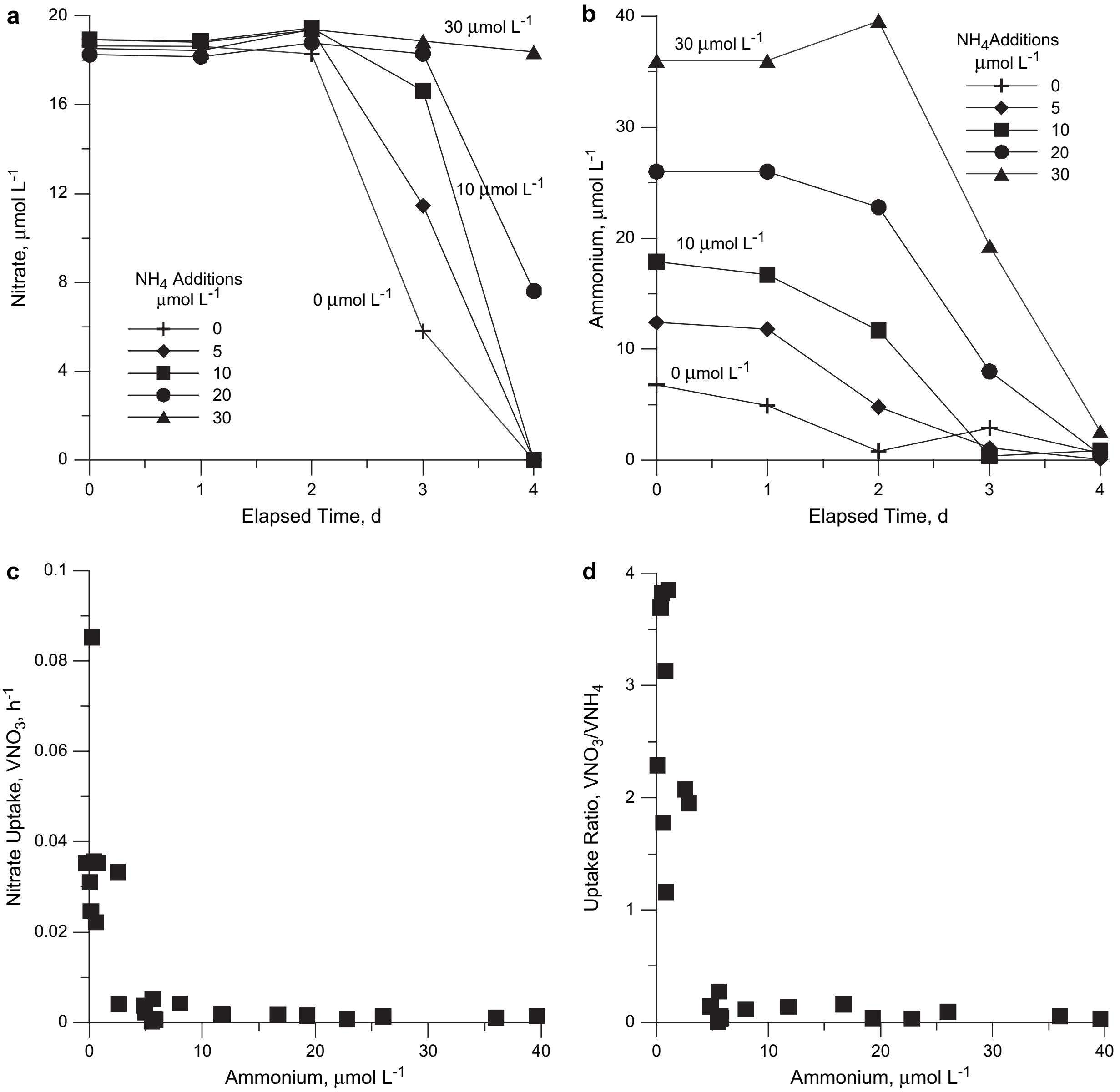


Fig. 8. Results from enclosures filled with Central Bay water in spring 2003 treated with NH_4 additions of 0, 5, 10, 20, 30 µmol L^{-1} and followed for 4 days. (a) NO_3, µmol L^{-1}, (b) NH_4, µmol L^{-1} plotted against elapsed time, (c) trace VNO_3, h^{-1}, (d) ratio of trace VNO_3:VNH_4 plotted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

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

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.

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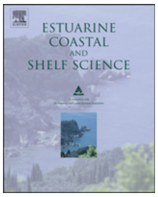

River flow and ammonium discharge determine spring phytoplankton blooms in an urbanized estuary

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ABSTRACT

Nutrient loadings to urbanized estuaries have increased over the past decades in response to population growth and upgrading to secondary sewage treatment. Evidence from the San Francisco Estuary (SFE) indicates that increased ammonium (NH_4) loads have resulted in reduced primary production, a counter-intuitive finding; the NH_4 paradox. Phytoplankton uptake of nitrate (NO_3), the largest pool of dissolved inorganic nitrogen, is necessary for blooms to occur in SFE. The relatively small pool of ambient NH_4, by itself insufficient to support a bloom, prevents access to NO_3 and bloom development. This has contributed to the current rarity of spring phytoplankton blooms in the northern SFE (Suisun Bay), in spite of high inorganic nutrient concentrations, improved water transparency and seasonally low biomass of bivalve grazers. The lack of blooms has likely contributed to deleterious bottom-up impacts on estuarine fish. This bloom suppression may also occur in other estuaries that receive large amounts of anthropogenic NH_4. In 2010 two rare diatom blooms were observed in spring in Suisun Bay (followed by increased abundances of copepods and pelagic fish), and like the prior bloom observed in 2000, chlorophyll accumulated after NH_4 concentrations were decreased. In 2010, low NH_4 concentrations were apparently due to a combination of reduced NH_4 discharge from a wastewater treatment plant and increased river flow. To understand the interactions of river flow, NH_4 discharge and bloom initiation, a conceptual model was constructed with three criteria; 1) NH_4 loading must not exceed the capacity of the phytoplankton to assimilate the inflow of NH_4, 2) the NH_4 concentration must be ≤ 4 µmol L^{-1} to enable phytoplankton NO_3 uptake, 3) the dilution rate of phytoplankton biomass set by river flow must not exceed the phytoplankton growth rate to avoid "washout". These criteria were determined for Suisun Bay; with sufficient irradiance and present day discharge of 15 tons NH_4–N d^{-1}at the upstream wastewater treatment plant (WTP). The loading criterion requires phytoplankton NH_4 uptake to exceed 1.58 mmol m^{-2} d^{-1}; the concentration criterion requires river flow >800 m^3 s^{-1} at the WTP for sufficient NH_4 dilution and the washout criterion requires river flow at Suisun Bay <1100 m^3 s^{-1}. The model and criteria are used to suggest how a reduction in anthropogenic NH_4, either by reduced discharge or increased dilution (river flow), could be used as a management tool to restore pre-existing productivity in the SFE and similarly impacted estuaries.

1. Introduction

Prior to 1987, phytoplankton blooms occurred regularly in spring and summer in the northern San Francisco Estuary (SFE) (Fig. 1). Ball and Arthur (1979) described the high chlorophyll conditions in Suisun Bay from 1969 to 1979 with mean chlorophyll concentrations of 30–40 µg L^{-1} in spring and 40–100 µg L^{-1} in summer. Diatoms were the dominant phytoplankton functional group. Phytoplankton blooms of this magnitude are now rare (Jassby, 2008), in spite of increasing inorganic nutrient concentrations delivered to Suisun Bay by the Sacramento River (Parker et al., 2012c). The zooplankton consumer trophic level is now food-limited (Müeller-Solger et al., 2002; Kimmerer et al., 2005). The lack of blooms has likely contributed to deleterious bottom-up impacts on estuarine fish by lowering the quantity and quality of food for the pelagic food web. Declines in four pelagic fish stocks and the listing of the delta smelt and longfin smelt as endangered and threatened species have been linked to the decline in phytoplankton in the northern SFE (Sommer et al., 2007),

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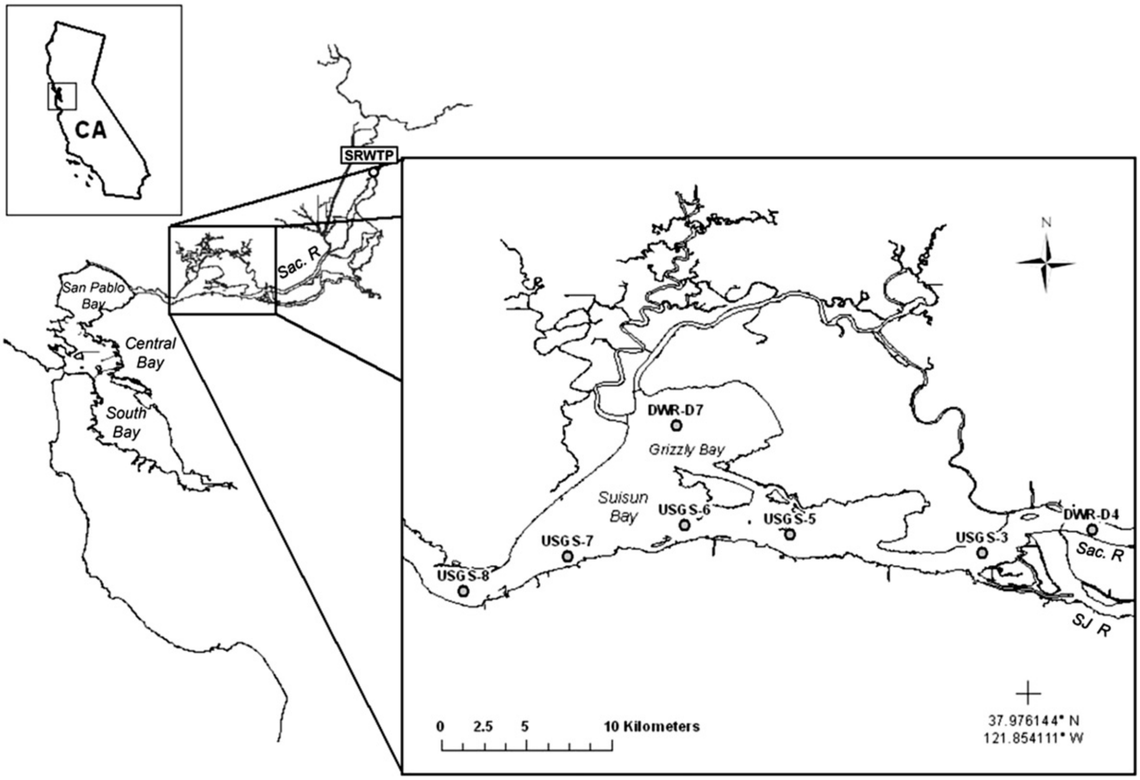

Fig. 1. Map of study site in northern San Francisco Estuary, California, USA showing the Sacramento Regional Wastewater Treatment Plant (SRWTP), Sacramento River (Sac. R), San Joaquin River (SJ. R) and the seven sampling stations in Suisun Bay.

a demonstration of the dependence of fishery yield on primary production (Nixon, 1988).

The decline in chlorophyll concentrations began in the early 1980's and blooms became rare after 1987, coincident with the introduction of an invasive clam, *Potamocorbula amurensis* (Alpine and Cloern, 1992; Jassby et al., 2002). The appearance of *P. amurensis* has been considered the major factor in the disappearance of phytoplankton blooms in Suisun Bay (Alpine and Cloern, 1988; Kimmerer and Orsi, 1996). However any role of *Potamocorbula* in eliminating phytoplankton blooms during spring is likely minor as clam biomass is low during that season (Greene et al., 2011). The lack of spring phytoplankton blooms in Suisun Bay suggests some other causal agent may suppress phytoplankton activity.

Since 1999, spring blooms have been observed only twice in Suisun Bay, in 2000 (Wilkerson et al., 2006; Kimmerer et al., 2012; Parker et al., 2012b) and recently in 2010 (during this study). A common feature of both blooms in which 30 $\mu g\ L^{-1}$ chlorophyll was measured, was a decline in ammonium (NH_4) concentrations to $\sim 1\ \mu mol\ L^{-1}$ (Wilkerson et al., 2006), suggesting a possible link between low NH_4 and bloom formation. Ammonium concentrations increased in the northern SFE and in Suisun Bay prior to the clam invasion, coincident with human population increase since the 1970's (Jassby, 2008; Glibert et al., 2011), reflecting increased wastewater discharge from the Sacramento Regional Wastewater Treatment Plant (SRWTP). The SRWTP currently discharges 15 tons N d^{-1}, largely as NH_4, to the inland delta of the SFE and to Suisun Bay (Jassby, 2008; his Fig. 1), a 3-fold increase from 5 tons N d^{-1} in 1987.

Elevated NH_4 from sewage effluent was implicated in depressed primary production along the California coast (MacIsaac et al., 1979), the Delaware Estuary (Yoshiyama and Sharp, 2006), the Scheldt Estuary (Cox et al., 2009), Wascana Creek, Canada (Waiser et al., 2010), and the inner bay of Hong Kong Harbor (Xu et al., 2010). At locations within the SFE, including Suisun Bay, elevated NH_4 has been linked to low chlorophyll, low rates of primary production and changes in phytoplankton community structure (Wilkerson et al., 2006; Dugdale et al., 2007; Glibert et al., 2011; Parker et al., 2012a,c).

The well-known inhibition of NO_3 uptake by NH_4 (e.g. Pennock, 1987) appears to be a key process and a likely causal agent leading to reduced primary production in environments with elevated NH_4 concentrations. In the SFE and the Sacramento River, phytoplankton NO_3 uptake is inhibited by NH_4 (Dugdale et al., 2007; Parker et al., 2012c). The lack of access to NO_3 limits primary production (Parker et al., 2012a,c) and the buildup of chlorophyll, i.e. blooms, since NO_3 is by far the largest component of the inorganic N pool, about 80% in Suisun Bay. The increased NH_4 may have also resulted in deleterious changes in the food web structure, e.g. diatoms replaced by cryptomonads and flagellates, large zooplankton replaced by smaller species (Glibert, 2010; Glibert et al., 2011).

Drawing from time-series data of chlorophyll, nutrient concentrations, phytoplankton nitrogen uptake (Wilkerson et al., 2006) and results from enclosure experiments (Dugdale et al., 2007; Parker et al., 2012a), the events leading to a spring phytoplankton bloom in SFE were shown to follow a predictable sequence (Dugdale et al., 2007; Parker et al., 2012a). In early spring, phytoplankton N demand in Suisun Bay is satisfied by NH_4 but with low biomass-specific and depth-integrated NH_4 uptake rates due to high turbidity and poor irradiance (Parker et al., 2012b). NO_3 uptake is low or near zero during this period due to NH_4 inhibition. With improved irradiance conditions (via increased water transparency, water column stability or seasonal increase in irradiance), phytoplankton NH_4 uptake rates and biomass increase causing water column NH_4 concentrations to decrease. Once NH_4 decreases to $<4\ \mu mol\ L^{-1}$ phytoplankton NO_3 uptake is enabled. With continued phytoplankton growth, NH_4 concentration is further

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reduced to $\leq$1 μmol L^{-1} and biomass-specific NO_3 uptake rates accelerate resulting in a rapidly developing bloom nourished by NO_3. However, if residence time is too low to allow the phytoplankton to assimilate the inflowing NH_4, as may happen with high river flow conditions or if there is very elevated NH_4 inflow, the production processes are only NH_4-based. NO_3 is unused and exported from the ecosystem (i.e. to the Pacific Ocean). Reduced primary production is a counter-intuitive result of elevated NH_4; the NH_4 paradox.

Here, we focus on a change in the chronically elevated NH_4 as a potential trigger for blooms in northern SFE; and those factors that may decrease the NH_4 concentration. A weekly sampling program was conducted during spring 2010 allowing a detailed examination to be made of the conditions that enabled the spring bloom to develop. The data are interpreted with respect to a conceptual model describing how NH_4 discharge from the SRWTP and flow in the Sacramento River may modulate nutrient conditions in Suisun Bay to allow a phytoplankton bloom (as occurred in 2000 and 2010) or to prevent blooms as in other years. These results contribute toward an understanding of the role of elevated anthropogenic NH_4 in estuarine primary productivity such that similar ecosystems with low productivity related to elevated NH_4 discharge could be successfully managed.

2. Conceptual model of nutrients, river flow and phytoplankton in Suisun Bay: criteria for phytoplankton blooms

2.1. Box model

A simple input/output model for Suisun Bay (herein "Bay") based on the sequence of bloom events described by Dugdale et al. (2007) was used to establish three criteria to evaluate when conditions are favorable for phytoplankton blooms. Fundamentally, the initial phytoplankton population must be capable of assimilating and controlling NH_4 input to the Bay so that NH_4 concentrations can be reduced sufficiently to enable NO_3 uptake. The critical variables of the NH_4 input are loading and concentration. 1) Loading to the Bay must not exceed the capacity of the phytoplankton to assimilate inflowing NH_4 (Loading Criterion) otherwise NH_4 concentrations within the Bay will increase. 2) The NH_4 concentration in the Bay must be $\leq$4 μmol L^{-1} or if the incoming concentration is >4 μmol L^{-1} then water residence time must be sufficient for the phytoplankton to reduce the concentration to <4 μmol L^{-1} (Concentration Criterion). 3) To avoid washout of the phytoplankton from the Bay before they can accumulate, the dilution rate of the Bay must not exceed the growth rate of the phytoplankton (Washout Criterion). If any of the criteria are not met, blooms will not form and the ecosystem will remain in a low productivity mode based solely on NH_4 uptake.

The variables needed to evaluate these criteria are NH_4 input to the river, river flow, and NH_4 uptake by the phytoplankton. From these variables, the parameters: loading, concentration, residence time and washout flow can be obtained by considering Suisun Bay as a box with surface area (A) of 1.7×10^8 m^2 and volume (V) of 9.9×10^8 m^3 with inflow from the Sacramento River that contains NH_4 from the SRWTP and outflow toward Suisun Bay and the northern SFE. River flow rates (F) were obtained from California Department of Water Resources Dayflow algorithm ("Delta Outflow" – www.water.ca.gov/dayflow/). Effluent NH_4 concentrations and effluent flow rate were obtained from SRWTP (SRWTP pers. comm.). First, the NH_4 input (discharge) as metric tons N d^{-1} or mmol N d^{-1} at the SRWTP (NH_4 input$_{(SRWTP)}$) is calculated from the NH_4 concentration in the effluent multiplied by the effluent flow.

$$NH_4 \text{ input}_{(SRWTP)} = [NH_4]_{\text{effluent}} {}^{*}\text{effluent flow} \quad (1)$$

Then the NH_4 input at the SRWTP (in mmol N d^{-1}) divided by the area of Suisun Bay (A) provides an estimate of the *potential loading* to the Bay:

$$\text{Potential loading to Suisun Bay}\left(\text{mmol N m}^{-2}\text{ d}^{-1}\right) = NH_4 \text{ input}_{(SRWTP)}/A \quad (2)$$

The *realized loading* will be lower than the *potential loading* due to *in situ* changes in the Sacramento River during its transit from SRWTP to Suisun Bay, e.g. by nitrification and phytoplankton uptake (Parker et al., 2012c). NH_4 concentrations decline downstream and NO_2 and NO_3 concentrations increase (e.g. Parker et al., 2012c), an indication of nitrification (Hager and Schemel, 1996). The NH_4 was observed to decrease downstream by 75% (Foe et al., 2010; Parker et al., 2012c; their Table 1) and this change must be applied to calculate *realized loadings* to Suisun Bay. Measurements of phytoplankton NH_4 uptake (4.65 mmol N m^{-2} d^{-1}) using ^{15}N–NH_4 and estimates of microbial nitrification (32.0–51.2 mmol N m^{-2} d^{-1}) indicated that the downstream decrease in NH_4 was due mostly to nitrification (Parker et al., 2012c). The nitrification rates were obtained using both a mass balance approach from increasing NO_3 concentrations downstream between SRWTP and Suisun Bay along with travel time, and also using an average specific nitrification factor (Yool et al., 2007) to predict the NO_3 produced from the ambient NH_4 in the river.

The *directly estimated loading* to Suisun Bay can also be obtained by calculating the NH_4 input to the Bay from the measured NH_4 concentration of the water entering the Bay multiplied by the flow into the Bay.

$$NH_4 \text{ input}_{(Suisun)} = [NH_4]_{\text{Suisun}} {}^{*}F \quad (3)$$

And then:

$$\text{Directly estimated loading to Suisun Bay}\left(\text{mmol N m}^{-2}\text{ d}^{-1}\right) = NH_4 \text{ input}_{(Suisun)}/A \quad (4)$$

Table 1

Calculated NH_4 concentration at the SRWTP discharge ($[NH_4]$ source) and Suisun Bay with varying effluent loads and Sacramento River flow rate. Ammonium loading to Suisun Bay is calculated with and without NH_4 loss (due to nitrification).

SRWTP effluent load tons NH_4–N d^{-1}	Flow rate m^3 s^{-1}	$[NH_4]$ source at SRWTP μmol L^{-1}	NH_4 inflow at Suisun Bay μmol L^{-1}	Loading to Suisun Bay mmol m^{-2} d^{-1}	
				Potential with no nitrification	*Realized* with nitrification
5	500	8.27	2.07	2.11	0.53
5	1000	4.13	1.03	2.11	0.53
5	2000	2.07	0.52	2.11	0.53
10	500	16.63	4.13	4.21	1.05
10	1000	8.27	2.07	4.21	1.05
10	2000	4.13	1.03	4.21	1.05
15	500	24.80	6.20	6.32	1.58
15	1000	12.40	3.10	6.32	1.58
15	2000	6.20	1.60	6.32	1.58

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The NH_4 concentration (in μmol L^{-1} = mmol m^{-3}) at the entrance to Suisun Bay ($[NH_4]_{(Susiun)}$) can be calculated using the NH_4 discharge at SRWTP and river flow (F) to calculate concentration at the source of discharge ($[NH_4]source_{(SRWTP)}$) that is then multiplied by 0.25 to allow for the 75% decrease in NH_4 downriver due to microbial nitrification (see Section 2.1 for rationale):

$$\begin{aligned}[NH_4]_{(Susiun)} &= [NH_4]source(SRWTP)*0.25 \\ &= (NH_4\ input(SRWTP)/F)*0.25 \qquad (5)\end{aligned}$$

To estimate the maximum river flow (F_{max}) allowed before dilution (D) results in no net phytoplankton growth for the Washout Criterion, Suisun Bay dilution is calculated as:

$$D\left(\text{as time}^{-1}\right) = F/V \qquad (6)$$

where F is river flow and V is volume of Suisun Bay ($9.9 \times 10^8\ m^3\ s^{-1}$). Then:

$$F = D*V \qquad (7)$$

From chemostat analogy, dilution (D) cannot be greater than phytoplankton growth rate – in this case the mean phytoplankton biomass-specific NH_4 uptake rate (VNH_4, time^{-1}).

So the washout point $D_{max} = VNH_4$

From Eqn. (7)

$$F_{max} = D_{max}*V = VNH_4*V = VNH_4*9.9 \times 10^8\ m^3\ s^{-1} \qquad (8)$$

At this flow and greater, there is no net growth of phytoplankton in the Bay, and the concentration of inflowing and outflowing phytoplankton biomass will be the same.

The interrelationships between NH_4 discharge, NH_4 concentration and river flow are shown as three hyperbolae (Fig. 2) calculated for discharges at the SRWTP of 15, 10 and 5 metric tons NH_4–N d^{-1} from Eqn. (5) relating river flow and NH_4 concentration. At any given river flow, the NH_4 concentration at the entrance to Suisun Bay increases as discharge increases (Eqn. (5)). The intersection of the solid horizontal line drawn from the NH_4 = 4 μmol L^{-1} with a discharge hyperbola indicates the minimum flow needed to dilute NH_4 concentration to 4 μmol L^{-1} (the Concentration Criterion). The washout threshold flow (F_{max}) is shown as the right-hand vertical dashed line on Fig. 2. The range of river flows within which bloom initiation can occur is set by this upper limit and a lower flow set by the discharge (vertical dotted lines). The window of flow rates contracts as the discharge increases, shown by the dotted vertical lines.

2.2. Calculating NH_4 loadings and concentrations

Using NH_4 discharges at SRWTP of 5, 10 and 15 tons NH_4–N d^{-1} (bracketing 1987 to present-day NH_4–N discharges, Jassby, 2008) and Eqn. (2), the *potential area-based loading* of NH_4 to Suisun Bay from the Sacramento River increased from 2.11 to 6.32 mmol m^{-2} d^{-1} over that period (Table 1). A reduction of 75% is applied to the discharge at SRWTP, to give *realized* (nitrification-corrected, see Section 2.1) *area-based NH_4 loadings* to Suisun Bay of 0.53 (when there was 5 tons NH_4–N d^{-1} discharge at SRWTP), to 1.58 mmol m^{-2} d^{-1} at 15 tons NH_4–N d^{-1} (present-day).

Three flow rates (500, 1000, and 2000 m^3 s^{-1}) and three NH_4 inputs at SRWTP (5, 10 and 15 tons NH_4–N d^{-1}) were used to calculate NH_4 concentration at the SRWTP discharge point and then at the entrance to Suisun Bay applying the 75% reduction due to nitrification (Table 1, Eqn. (5)). Ammonium concentrations at a given flow rate increase as the discharge rate increases. This analysis does not include when the flow into Suisun Bay is not equal to the flow at the SRWTP which occurs when water is diverted from the Sacramento for agricultural and domestic use. Also, additional sources of NH_4 (e.g. other WTPs) were not included in these calculated loadings as it is assumed here that SRWTP represents the only NH_4 source to Suisun Bay. It has been shown that SRWTP as a point source supplies 90% of the NH_4 (Jassby, 2008) in the northern SFE. Present-day nutrient inventories for the Sacramento River and Suisun Bay are incomplete but Hager and Schemel (1992) suggest that agricultural sources are minor downstream of the SRWTP and the location of nonpoint source of nutrients is unclear and likely to have insignificant inputs.

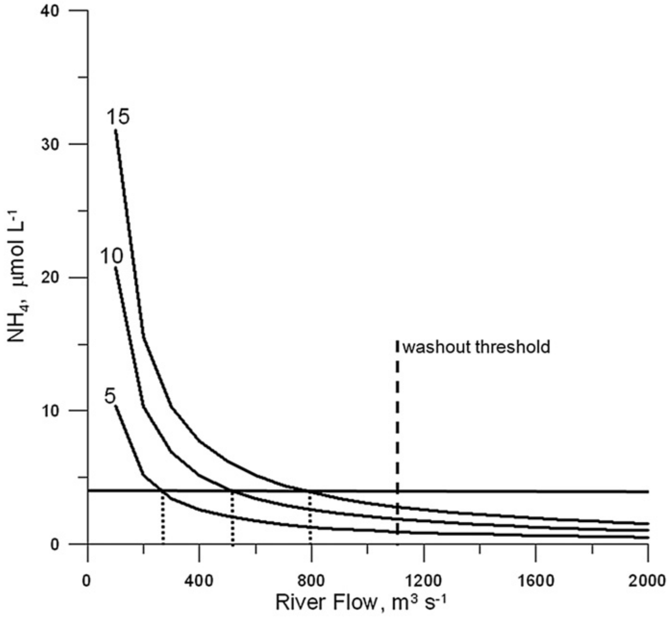

Fig. 2. Ammonium concentration of inflowing river water at the entrance to Suisun Bay as a function of river flow at point of discharge and three effluent discharge levels (5. 10 and 15 tons NH_4–N d^{-1}). The 3 dotted vertical lines show the river flow that will result in NH_4 = 4 μmol L^{-1} at Suisun Bay for each of three discharge levels. The dashed vertical line shows the washout criterion at which the phytoplankton population washes out.

2.3. Obtaining values for the three criteria

2.3.1. Loading Criterion

To evaluate the Loading Criterion (i.e. that NH_4 loading must not exceed the NH_4 uptake capacity of the phytoplankton), peak and non-peak phytoplankton NH_4 uptake rates were used to evaluate whether Suisun Bay phytoplankton have the capacity to keep pace with potential NH_4 loading. The mean phytoplankton NH_4 uptake during spring in Suisun Bay measured from 1999 to 2003 was 0.032 mmol m^{-3} h^{-1} (Wilkerson et al., 2006) and the peak value was 0.074 mmol m^{-3} h^{-1} (unpublished data). These hourly rates were converted to daily rates (*24) and then depth-integrated values were obtained (0.88 mmol m^{-2} d^{-1} and 2.02 mmol m^{-2} d^{-1}) assuming uniform uptake throughout the euphotic zone and estimating euphotic zone from the mean spring Secchi depth measured in Suisun of 0.3 m (Wilkerson et al., 2006) using the relationship in Cole and Cloern (1987). Comparison of the historical NH_4 discharges to Suisun Bay with the mean and peak phytoplankton NH_4 uptake rates (0.88 mmol m^{-2} d^{-1} and 2.02 mmol m^{-2} d^{-1}) indicates that the discharge of 10 tons NH_4–N d^{-1} and the current 15 tons NH_4–N d^{-1} exceed the mean capacity of the Suisun Bay phytoplankton to absorb the input of NH_4 (Table 1). With discharge of 15 tons NH_4–N d^{-1} phytoplankton uptake rate must exceed 1.58 mmol m^{-2} d^{-1} (Table 1). In order to change the balance in favor of phytoplankton

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bloom formation, either NH_4 loading would need to decrease or the phytoplankton NH_4 uptake rate would need to increase (to the peak value). At the 5 tons NH_4–N d^{-1} discharge in 1987, the phytoplankton uptake would have been capable of absorbing the NH_4 input.

2.3.2. *Concentration Criterion*

The second criterion (Concentration Criterion) for rapid NO_3-based bloom initiation requires an NH_4 concentration of ≤ 4 μmol L^{-1}. The concentrations calculated for Suisun Bay (allowing for 75% reduction between the SWRTP and Suisun Bay due mostly to nitrification-see Section 2.1) (Table 1) suggest that this criterion is met at present-day discharge at flows of 1000 and 2000 m^3 s^{-1}. At 500 m^3 s^{-1}, the calculated inflowing NH_4 concentration is 6.2 μmol L^{-1}, in excess of the required 4 μmol L^{-1}. In Fig. 2, a line drawn from the *y*-axis at a concentration of 4 μmol L^{-1} is the upper boundary for the Concentration Criterion. The intersection of that line with a discharge hyperbola indicates the minimum flow required to meet the Concentration Criterion indicated by the vertical line intersecting the *x*-axis. As discharge increases, the necessary river flow increases. At the present discharge, 15 tons NH_4–N d^{-1}, flow of at least 800 m^3 s^{-1} is required.

2.3.3. *Washout Criterion*

The washout threshold flow (F_{max}), shown as the right-hand vertical dashed line on Fig. 2, is based on the mean biomass-specific NH_4 uptake rate for Suisun Bay in spring, 0.004 h^{-1} (Wilkerson et al., 2006). From Eqn. (8)

$$F_{max} = 0.004\ h^{-1} * 9.9 \times 10^8\ m^3 = 1100\ m^3\ s^{-1} \qquad (9)$$

The range of river flows within which bloom initiation can occur is set by this upper limit and a lower flow set by the discharge. The window of flow rates contracts as the discharge increases and at present discharge (15 metric tons NH_4–N d^{-1}) is relatively narrow (i.e. 800–1100 m^3 s^{-1}).

In summary, for bloom initiation, besides sufficient irradiance, if the discharge at SRWTP is the present day value of 15 tons NH_4–N d^{-1}, Criterion 1 (Loading Criterion) requires that the phytoplankton NH_4 uptake rate must exceed 1.58 mmol m^{-2} d^{-1}; Criterion 2 (Concentration Criterion, $NH_4 = \sim 4$ μmol L^{-1} at Suisun Bay) requires river flow >800 m^3 s^{-1} at the SRWTP for sufficient dilution and Criterion 3 (Washout Criterion) requires river flow at Suisun Bay <1100 m^2 s^{-1}. The river flow, discharge and loading conditions during spring 2010 were evaluated to establish if any of these criteria were met to allow bloom initiation.

3. Site description and methods

Seven stations were sampled in the main channel ($\sim$10 m depth) of Suisun Bay along with a single shoal station ($<$2 m depth: DWR-D7), on 17, 24 March; 7, 14, 26 April; 12, 24 May and 16, 21 June 2010 (Fig. 1). At each station measurements of water transparency were made with a Secchi disk, and temperature and salinity with a YSI-6920 sonde. Salinity was measured using the Practical Salinity Scale. Surface water was sampled with a clean bucket for concentrations of nutrients and chlorophyll as well as enumeration of phytoplankton species.

The sampled water was filtered through clean precombusted (450 °C, 4-hr) 25 mm Whatman GF/F filters and the filtrate collected for nutrient analyses. Twenty-ml filtered samples were analyzed using a Bran and Luebbe AutoAnalyzer II with MT-19 manifold chemistry module for $NO_3 + NO_2$ and NO_2 according to Whitledge et al. (1981) and Bran and Luebbe Method G-172-96 (Bran Luebbe, 1999a), phosphate (PO_4) according to Bran and Luebbe Method G-175-96 (Bran Luebbe, 1999b) and silicate ($Si(OH)_4$) by Bran and Luebbe Method G-177-96 (Bran Luebbe, 1999c). $NO_3 + NO_2$ is referred to as NO_3 throughout the text as NO_2 concentrations were very low ($<$1.0 μmol L^{-1}). Twenty-five ml filtered samples were analyzed for NH_4 according to Solorzano (1969). Samples for chlorophyll were prepared in the field by filtering 50 mls of sample water onto 25 mm Whatman GF/F filters. Chlorophyll on the filters was determined by *in vitro* fluorometry after extraction in 90% acetone using a Turner 10AU fluorometer (Arar and Collins, 1992) calibrated with commercially available chlorophyll (Turner Designs) and corrected for phaeophytin by hydrochloric acid addition (Holm-Hansen et al., 1965). Water was sampled in 250-ml amber glass bottles and preserved with Lugols iodine for phytoplankton enumeration, using the Utermohl settling technique (Utermohl, 1958) with 25-ml chambers and inverted microscopy. Phytoplankton were identified to genus. Laboratory quality assurance/quality control followed the Surface Water Ambient Monitoring Program (SWAMP) protocols set by the California State Water Resources Control Board (http://www.waterboards.ca.gov/water_issues/programs/swamp/qamp.shtml). This included implementation of standard laboratory procedures including replicates, field blanks, matrix spikes, certified reference materials, setting of control limits, criteria for rejection, and data validation methods. All analyses were carried out on fresh samples within 24 h of collection.

4. Results

4.1. *Field observations of chlorophyll, nutrients and phytoplankton*

When sampling began on 17 March, 2010, NH_4 concentrations were high, (6.8–10.3 μmol L^{-1}) with the maximum value at the most upstream location, at the entrance to Suisun Bay, DWR-D4 (Figs. 1 and 3a) and chlorophyll concentrations were uniformly low (1.4–3.4 μg L^{-1}). By 24 March, chlorophyll concentrations increased (2.8–4.3 μg L^{-1}) and NH_4 concentrations were relatively unchanged (Fig. 3b) except for DWR-D4 where NH_4 had declined substantially. Two weeks later, 7 April, chlorophyll concentrations had increased (3.7–7.4 μg L^{-1}) at all but the two most downstream stations (Fig. 3c). NH_4 concentrations had declined at all stations except DWR-D4. The lowest NH_4 concentrations were found at the mid Suisun Bay stations, USGS 5 and USGS 6 (4.4 and 3.7 μmol L^{-1}, respectively) and the shoal station DWR-D7 (3.4 μmol L^{-1}). Station DWR-D4 had elevated NH_4 compared to the other stations.

One week later, 14 April, a phytoplankton bloom was observed in mid Suisun Bay (USGS 5) with a chlorophyll concentration of 30.9 μg L^{-1}. NH_4 concentrations at this station were 1.7 μmol L^{-1} (Fig. 3d) and were consistently low across stations in mid Suisun Bay. The highest NH_4 concentration (8.6 μmol L^{-1}) occurred at USGS 7, located in western Suisun Bay adjacent to the Central Contra Costa Sanitation District WTP outfall. Chlorophyll concentrations were low (1.9 μg L^{-1} and 1.5 μg L^{-1}) at USGS 7 and the next downstream station, USGS 8.

On 26 April, there was a clear U-shaped pattern of NH_4 concentration within Suisun Bay with a minimum at USGS 5 (Fig. 3e). A mirror image pattern of chlorophyll was also observed (Fig. 3e) with the lowest chlorophyll upstream and downstream and the maxima at USGS 5 (21 μg L^{-1}) and the shoal station (DWR-D7, 20 μg L^{-1}). By May 12, the bloom had largely faded although substantial chlorophyll concentrations (5–10 μg L^{-1}) still remained at all but the two downstream stations where the highest NH_4 concentrations (5.2 and 7.2 μmol L^{-1}) were measured (Fig. 3f).

Two weeks later, 24 May, a second, larger phytoplankton bloom both in magnitude and spatial extent had developed, with

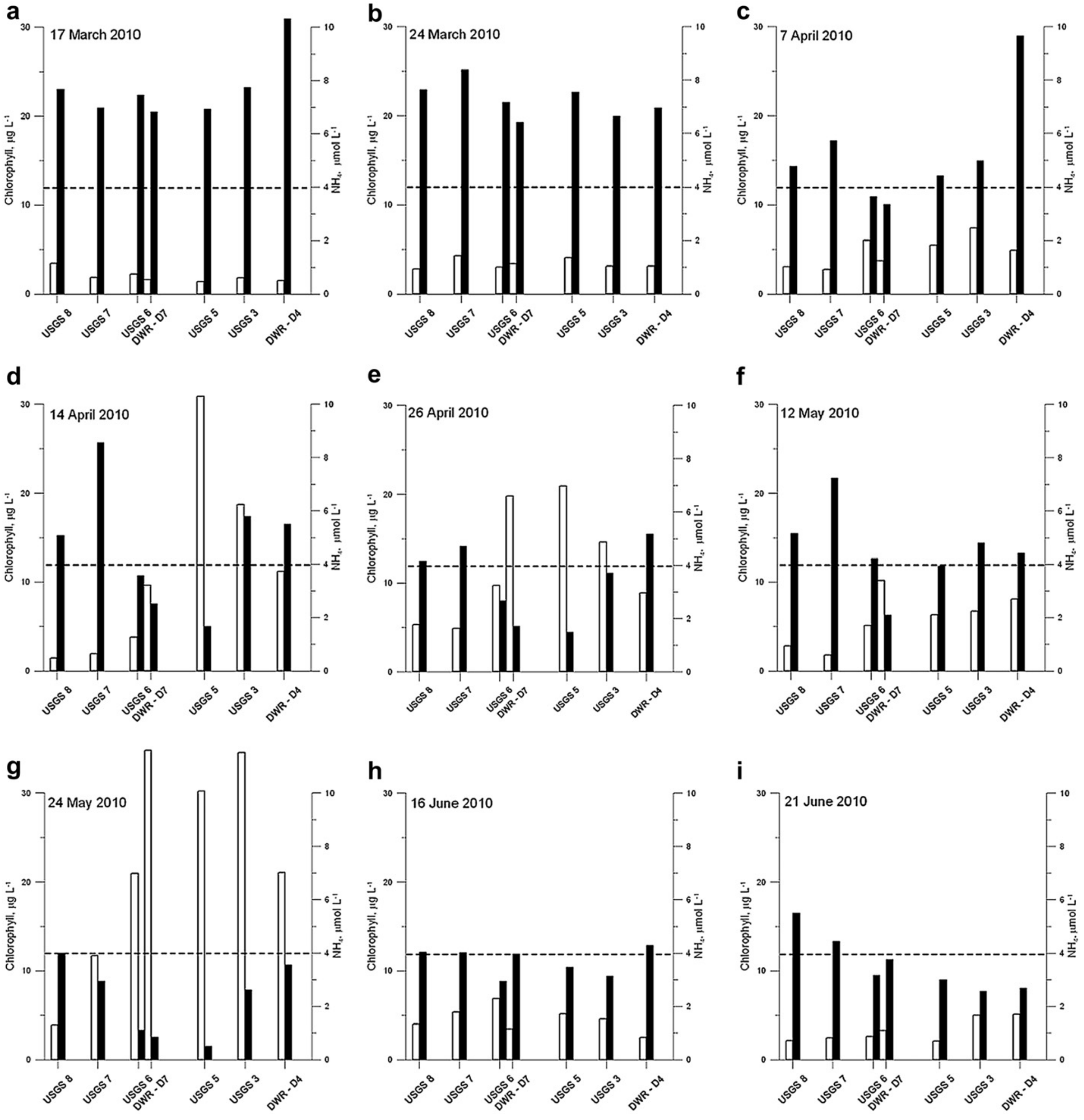

Fig. 3. Chlorophyll (white bars) and NH_4 concentrations (black bars) at the seven sampling locations measured in 2010 on a) 17 March, b) 24 March, c) 7 April, d) 14 April, e) 26 April, f) 12 May, g) 24 May, h) 16 June and i) 21 June. The dashed lines show $NH_4 = 4$ µmol L^{-1}. DWR-D7 is not located on the Suisun Bay transect but lies to the north of USGS 6 so is plotted next to USGS 6.

chlorophyll up to 34 µg L^{-1} at all but the two downstream stations, USGS 7 and USGS 8 (Fig. 3g). Ammonium concentrations were ≤ 1 µmol L^{-1} at mid-Bay stations including DWR-D7, and <4 µmol L^{-1} at the most upstream station (DWR-D4). By 16 June, chlorophyll had declined to between 2.5 and 6.9 µg L^{-1} within the study area and NH_4 concentrations were ~4 µmol L^{-1} (Fig. 3h). One week later, 21 June, chlorophyll concentrations had declined further (2–5 µg L^{-1}) and a pattern of NH_4 concentration (2.5–5.5 µmol L^{-1}) increasing downstream was apparent (Fig. 3i).

The spatial and temporal patterns in chlorophyll and NH_4, along with NO_3, $Si(OH)_4$ and PO_4 are shown also as contours on a location (DWR-D4 in Suisun Bay to USGS 8 near San Pablo Bay) versus time plane in Fig. 4a–e. The two blooms (end of April and May) were centered at USGS 3 to USGS 5 (Fig. 4a). These blooms occurred on the upstream side of the 2 isohaline (Fig. 4a). NH_4 concentration (Fig. 4b) declined through mid-Bay but increased again at USGS 7, with an NH_4 minimum (<4 µmol L^{-1}) corresponding closely to the chlorophyll maximum distribution with time. NO_3 concentrations

(Fig. 4c) declined with time from about 35 to 10 μmol L^{-1}, the latter coincident with the second bloom. Phosphate and $Si(OH)_4$ concentrations declined as spring progressed with lower values observed during the periods of both blooms (Fig. 4d, e). A $Si(OH)_4$ minimum was associated with the second bloom. At DWR-D4 the Secchi depth varied little with a mean of 0.6 ± 0.2 m and the mean salinity was low, 0.14 ± 0.07 (Table 2).

Diatoms made up virtually all of the phytoplankton counted (Fig. 5). The abundances of the five most common diatoms at three channel stations, DWR-D4, USGS 3, USGS 5 and at the shoal station, DWR-D7 are plotted for five sampling dates in 2010; 24 March, 7, 14 and 26 April and 24 May (Fig. 5). The first bloom in April (Fig. 5c) was dominated by the pennate diatom *Entomoneis* (synonym: *Amphiprora*; http://westerndiatoms.colorado.edu) and the second on 24 May (Fig. 5e) by the long-chain centric diatom *Melosira* Fig. 5a–d). *Entomoneis* (a tychopelagic diatom that is normally benthic; Cupp, 1943) occurred persistently in the shoal and downstream region of Suisun Bay, while centric pelagic diatoms (*Cyclotella* and *Melosira*) were upstream (Fig. 5a–d). Diatom dominance in the two blooms is consistent with the concurrent decline in $Si(OH)_4$ and increased chlorophyll (Fig. 4).

4.2. NH_4 loading to Suisun Bay, NH_4 concentrations in Suisun Bay and river flow in spring 2010

4.2.1. Loading

Discharge of NH_4 at SRWTP (Fig. 6a) was calculated from effluent concentrations and effluent flow at the SRWTP and normalized to the surface area of Suisun Bay (Eqns. (1) and (2)). In the period 17 March to 7 April *potential loading* varied from 5.24–6.61 mmol m^{-2} d^{-1} (Table 2), then remained ~6 mmol m^{-2} d^{-1} through 12 May and then declined to 5.59 mmol m^{-2} d^{-1} on 24 May. The mean NH_4 loading for the period 17 March to 24 May, 5.86 ± 0.52 mmol $m^{-2}d^{-1}$ is not distinguishable from the loading with a discharge rate of 15 tons NH_4–N d^{-1}, 6.32 mmol m^{-2} d^{-1} (Table 1). When *realized loading* at the entrance to Suisun Bay was estimated by application of a 75% reduction due to nitrification (see section 2.1), the values (Table 2) fall within the range of the Loading

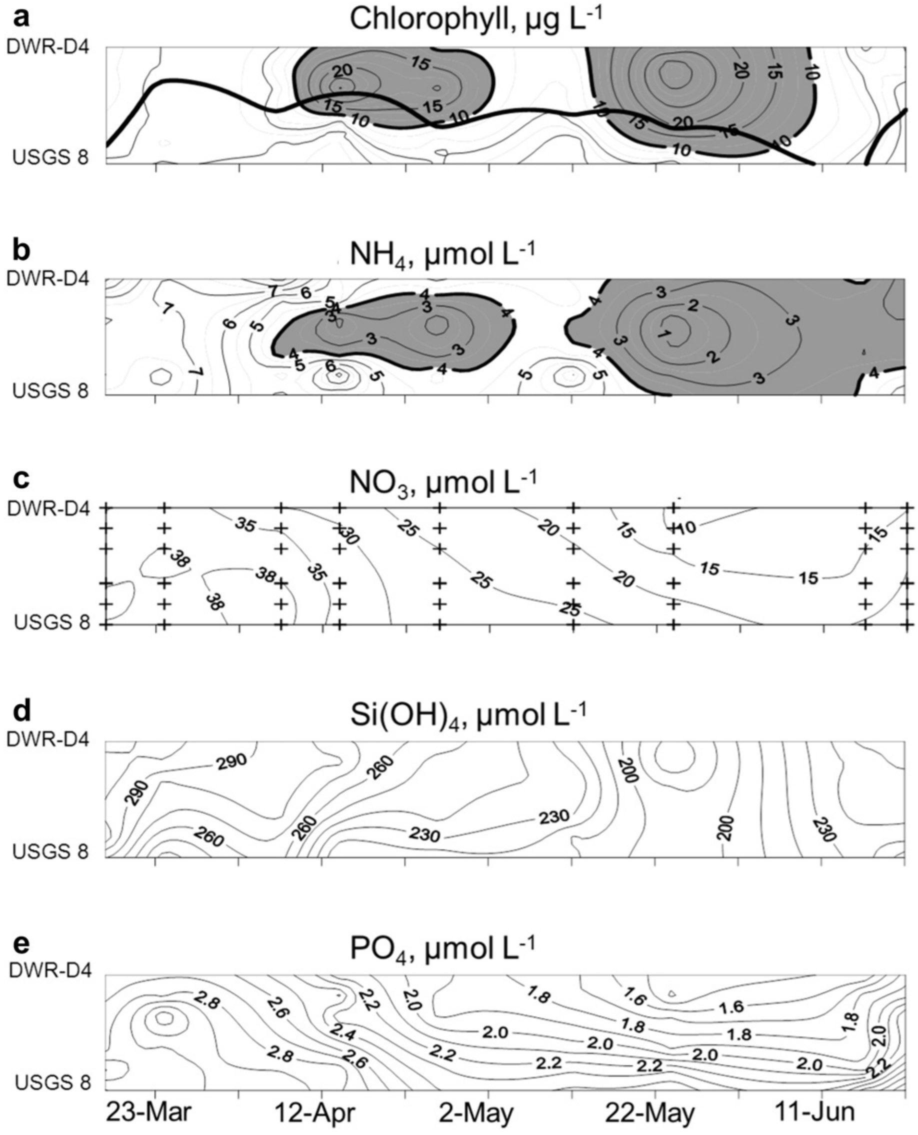

Fig. 4. Surface contours of concentrations of nutrients and chlorophyll plotted versus sampling location on the Suisun Bay transect (*y*-axis) from USGS 8 (downstream) to DWR-D4 (upstream) and time (*x*-axis). DWR-D7 is not included. a) Chlorophyll with areas >10 μg L^{-1} shaded in grey. The 2 salinity isohaline is overlaid as a bold black line. b) NH_4 with areas <4 μmol L^{-1} shaded in grey, c) NO_3, d) $Si(OH)_4$, e) PO_4. Crosses on c) show the sampling locations.

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Table 2
Secchi depth, salinity and NH_4 concentration at Suisun Bay (i.e. DWR-D4) with Delta Outflow used to calculate *directly estimated NH_4 loading* to Suisun Bay, and river flow at SRWTP used to calculate NH_4 concentration and *potential loading* at SRWTP and *realized NH_4 loading* to Suisun Bay from the NH_4 discharge at SRWTP. No discharge data available for June 2010, so no calculated values.

Date 2010	Secchi depth m	Salinity	Delta Outflow $m^3\ s^{-1}$	Measured NH_4 at Suisun µmol L^{-1}	*Directly estimated NH_4 loading* to Suisun mmol $m^{-2}\ d^{-1}$	Calc NH_4 at Suisun µmol L^{-1}	*Realized NH_4 loading* to Suisun mmol $m^{-2}\ d^{-1}$	River flow at SRWTP $m^3\ s^{-1}$	Calc NH_4 at SRWTP µmol L^{-1}	*Potential NH_4 loading* at SRWTP mmol $m^{-2}\ d^{-1}$
17 March	0.50	0.13	395.1	10.31	2.08	5.20	1.31	495.3	20.78	5.24
24 March	0.50	0.30	262.5	6.97	0.93	6.68	1.31	384.9	26.73	5.25
7 April	1.00	0.18	567.0	9.66	2.79	7.74	1.65	418.9	30.95	6.61
14 April	0.75	0.14	759.7	5.50	2.13	5.16	1.56	591.6	20.63	6.22
26 April	0.50	0.11	709.8	5.18	1.87	5.36	1.49	546.3	21.45	5.97
12 May	0.50	0.11	604.8	4.43	1.36	6.98	1.54	433.1	27.90	6.15
24 May	0.25	0.11	503.7	3.56	0.91	6.50	1.40	421.7	26.00	5.59
16 June	0.50	0.07								
21 June	0.50	0.08								
Mean ± s.d.	0.56 ± 0.21	0.14 ± 0.07	543.2 ± 173.8	6.52 ± 2.59	1.73 ± 0.69	6.23 ± 1.01	1.47 ± 0.13	470.3 ± 76.1	24.92 ± 4.03	5.86 ± 0.52
17 Mar–7 Apr mean ± s.d.	0.67 ± 0.29	0.20 ± 0.09	408.2 ± 152.7	8.98 ± 1.77	1.93 ± 0.94	6.54 ± 1.28	1.43 ± 0.20	433.1 ± 56.5	26.15 ± 5.11	5.70 ± 0.79
14 Apr–24 May mean ± s.d.	0.50 ± 0.20	0.12 ± 0.02	644.5 ± 113.9	4.67 ± 0.86	1.57 ± 0.54	6.00 ± 0.88	1.50 ± 0.07	498.2 ± 83.9	24.00 ± 3.52	5.98 ± 0.28

Criterion defined by mean and peak NH_4 uptake (Fig. 6a, horizontal dotted lines).

Using the discrete measurements of NH_4 concentrations at DWR-D4 (entrance to Suisun Bay) and Delta Outflow, a more direct estimate of the NH_4 loading to Suisun Bay for the same period in spring 2010 was calculated (Eqns. (3) and (4)). This *directly estimated NH_4 loading* declined from 2.79 mmol $m^{-2}\ d^{-1}$ on 7 April prior to the bloom period, to 0.91 mmol $m^{-2}\ d^{-1}$ at the end of the bloom period (Table 2, Fig. 6a). During the bloom period, it fell within the Loading Criterion range (only slightly above the peak criterion line on 12 April) (Fig. 6a). The overall mean *directly estimated NH_4 loading* from March through May (1.73 ± 0.69 mmol $m^{-2}d^{-1}$)(Table 2), is close to the value estimated assuming 15 tons NH_4–N d^{-1} discharge at the WTP discharge location after accounting for nitrification losses of NH_4, 1.58 mmol $m^{-2}d^{-1}$ (Table 1).

4.2.2. Ammonium concentrations

Although changes in river flow at SRWTP do not affect the calculated NH_4 loading to Suisun Bay (with no export pumping), changes in flow at SRWTP affect the concentration of NH_4 in the river as a result of dilution and these changes are propagated downstream. A rapid change in concentration (calculated from the SRWTP discharge and flow) occurred at SRWTP between 7 and 14 April when NH_4 concentration declined by ~30% from 30.95 to 20.63 µmol L^{-1} (Table 2, Fig. 6b). The discharge at SRWTP decreased only slightly from 6.61–6.22 mmol $m^{-2}\ d^{-1}$ between these dates and could not have caused such a change in concentration at SRWTP (Table 2, Fig. 6b). The change in concentration was the result of rapid increase in flow at the SRWTP (from 418.9 to 591.6 $m^3\ s^{-1}$) (Fig. 6b, Table 2). Between 7 and 14 April the calculated NH_4 concentrations at DWR-D4 also declined, from 7.74 to 5.16 µmol L^{-1} (Table 2) and the measured concentration of NH_4 declined nearly 50% from 9.66 to 5.50 µmol L^{-1} as river flow at DWR-D4 (i.e. Delta Outflow) increased from 567.0–759.7 $m^3\ s^{-1}$.

Both measured and calculated NH_4 concentrations at DWR-D4 fell slightly above the Concentration Criterion, 4 µmol L^{-1}, with measured concentrations near the criterion value from the first bloom period in April to the second bloom in late May. The overall mean NH_4 concentration (6.52 ± 2.59 µmol L^{-1}) that was measured at the overall mean river flow (543.2 ± 173.8 $m^3\ s^{-1}$, Table 2) is in good agreement with the predicted NH_4 concentrations at the entrance to Suisun Bay assuming 15 tons NH_4–N d^{-1} discharge and 500 m s^{-1} river flow (6.20 µmol L^{-1},Table 1) at DWR-D4.

4.2.3. Washout flow

The highest river flow at DWR-D4, on April 14, 759.7 $m^3\ s^{-1}$ (Table 2), was well below the present Washout Criterion threshold, 1100 $m^3\ s^{-1}$. For the rest of the period flows into Suisun Bay were about 50% of the washout thresholds.

5. Discussion

5.1. Overview

Two diatom blooms were observed in Suisun Bay in spring 2010. Ammonium loading was within the criteria limits set by mean and peak NH_4 uptake capacity of the phytoplankton. NH_4 concentrations in Suisun Bay in April were near the Concentration Criterion (4 µmol L^{-1}) predicted to enable blooms. Washout was clearly avoided and river flow was below the current Washout flow Criterion. The major trigger was a sudden decline in both measured and predicted NH_4 concentration at the entrance to Suisun Bay (DWR-D4), the result of rapid increases in flow at both SRWTP and Delta Outflow (Fig. 6b, Table 2). Ammonium concentrations continued to decline throughout the bloom period to about 1 µmol L^{-1} (Figs. 3 and 4). The 2010 bloom followed the sequence described by Dugdale et al. (2007) in which NH_4 initially declined and chlorophyll biomass started to increase. When NH_4 concentration was reduced to 1 µmol L^{-1} NO_3 was used and chlorophyll biomass increased rapidly.

5.2. The NH_4 paradox

The observation that high NH_4 concentrations, in the presence of ample NO_3, results in reduced algal productivity is counterintuitive and requires explanation, since it is well known that when most algae are grown in batch culture on a medium containing both NH_4 and NO_3, NH_4 will be taken up first and when exhausted NO_3 will be taken up. The physiological process that reduces or eliminates phytoplankton NO_3 use is generally referred to as NH_4 inhibition of NO_3 uptake (e.g. Eppley et al., 1979; Dortch, 1990; Cochlan and Bronk, 2003) and may occur at NH_4 concentrations as low as 0.1–0.3 µmol L^{-1} (Wheeler and Kokkinakis, 1990).

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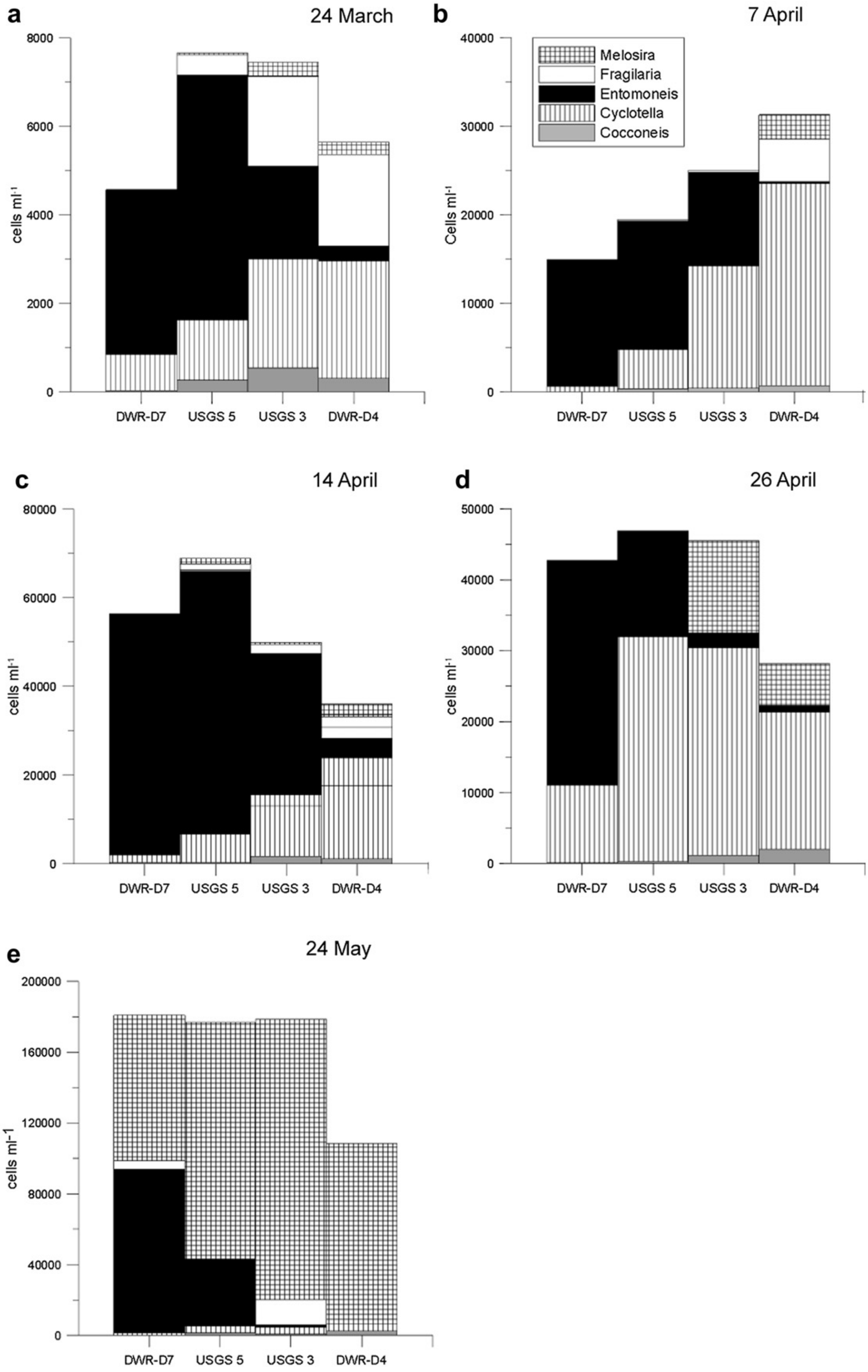

Fig. 5. Cell concentration (cells ml^{-1}) of the most abundant diatom species (from bottom: *Cocconeis*, *Cyclotella*, *Entomoneis*, *Fragilaria*, *Melosira*) at three channel stations and one shoal station (DWR-D7) collected in 2010 on a) 24 March, b) 7 April, c) 14 April, d) 26 April and e) 24 May.

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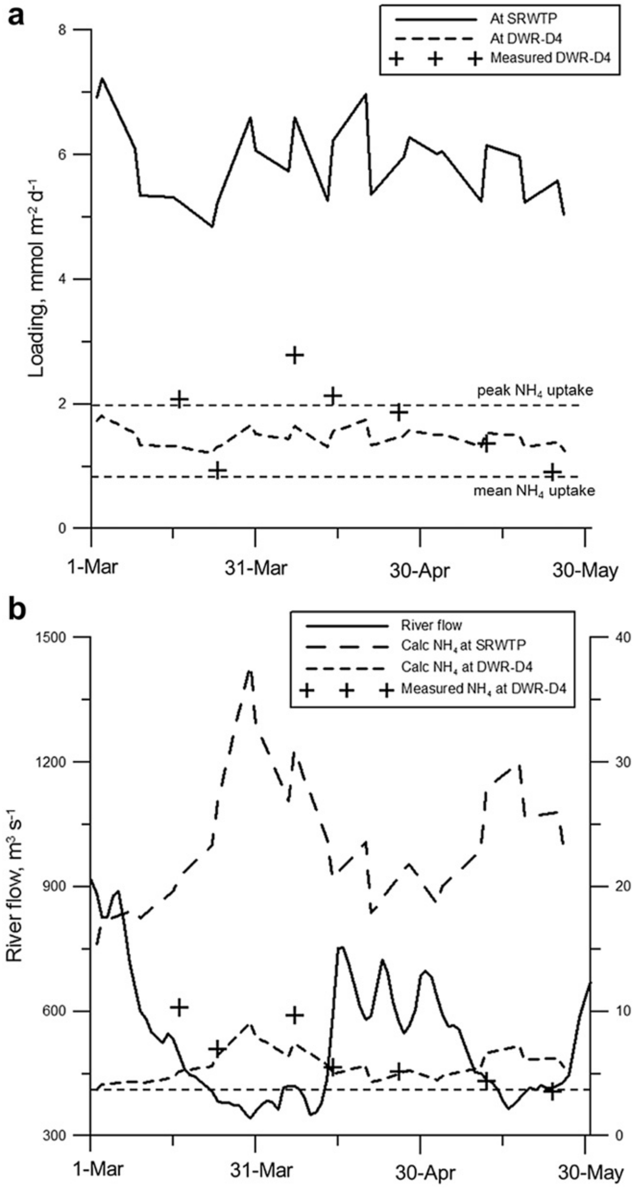

Fig. 6. a). Ammonium loading calculated at SRWTP and at station DWR-D4 (entrance to Suisun Bay) from discharge and river flow; DWR-D4 loading values (in crosses) calculated using NH_4 concentration at DWR-D4 and Delta Outflow, overlaid with horizontal dotted lines with mean and peak phytoplankton NH_4 uptake rates for Suisun Bay indicating the loading criterion to be met. b) River flow at the SRWTP with calculated (predicted) NH_4 concentration at SRWTP and DWR-D4, and measured NH_4 at DWR-D4 (crosses). The concentration criterion of 4 µmol L^{-1} is shown as a horizontal dotted line.

When both NH_4 and NO_3 are fully assimilated, the yield of algae is the sum of the commonly considered inorganic nitrogen forms (typically NH_4 plus NO_3). In a lake or lagoon, the progression of NH_4 and NO_3 uptake and algal production would follow that of the laboratory culture flask, providing no other nutrient becomes limiting. However, in a river or estuary, nutrients are refreshed from source regions by flow and the relative proportions of NH_4 and NO_3 become important. For example, consider source water flowing into a bay containing a 50:50 mixture of NH_4 and NO_3, 20 µmol L^{-1} in each component. If the flow rate is low enough to allow phytoplankton biomass to accumulate and take up first all NH_4 and then all NO_3, 40 µmol L^{-1} of phytoplankton N will be produced. This is equivalent to 40 µg L^{-1} chlorophyll (1 µmol N removed produces ~1 µg L^{-1} chlorophyll; see Dugdale and Goering, 1970; Marra et al., 1990 and refs therein). However, if the flow is sufficiently high to prevent full biomass accumulation (i.e. residence time is short), NH_4 may remain at concentrations sufficient to block NO_3 uptake. The 20 µmol L^{-1} of NO_3 is unused and flows out of the system. The maximum phytoplankton biomass (~chlorophyll) would depend only on the NH_4 taken up, a maximum of 20 µmol L^{-1} NH_4 in the inflowing source water (a maximum of 20 µg L^{-1} chlorophyll). In this way, high NH_4 results in less than maximal chlorophyll and productivity.

5.3. *Diatom contribution and distribution*

Diatoms made up virtually all of the phytoplankton (72–100% of the phytoplankton counted) during the bloom periods, consistent with recent phytoplankton studies in the SFE (Cloern and Dufford, 2005) and with historic studies (Ball and Arthur, 1979). The diatoms observed included benthic *Cocconeis* and *Entomoneis*. Lidstrom (2008) also observed an abundance of *Entomoneis* in Suisun Bay in 2007. Two of the dominant diatom genera described in Ball and Arthur (1979), *Melosira* and *Cyclotella*, were also dominant in the Suisun 2010 bloom. From Fig. 3a–e it appears that the April 2010 bloom began in the channel of the central part of Suisun Bay and then was observed at the shoal station.

5.4. *Comparison of 2009 and 2010*

No bloom was observed in 2009 and some comparisons can be made for 2009 with criteria parameters and environmental conditions during the bloom year 2010. Loading Criteria for 2009 compared to 2010 can be evaluated from average April SRWTP discharge rates. No direct estimates of loading at DWR-D4 are available since no detailed sampling of Suisun Bay was made in 2009. The average discharge of NH_4 from SWRTP declined by 7% in 2010 compared to 2009, and the loading to Suisun Bay declined by the same amount (Table 3).

The average river flow rate at SRWTP in April was 50% higher in 2010 compared to 2009 (Fig. 7a, Table 3). The temporal pattern of flow also was different in the March to May periods of the two years. In 2009 flow declined to a low level and remained low until a single peak in early May. In 2010, a March low flow was followed by a sharp increase in mid-April declining by the end of May, the flow increase thought to be the trigger for the 2010 bloom. The effect of different flow patterns is shown by the trends in NH_4 concentration at the effluent discharge location from March to June of 2009 and 2010 (Fig. 7b). The decline in NH_4 concentration in 2010 in April does not occur in 2009 due to the lack of increased flow in April 2009.

Table 3
Mean (±s.d.) flow, effluent discharge and calculated NH_4 concentration at SRWTP in April 2009 and 2010, and *realized loading* and calculated NH_4 concentration at entrance to Suisun Bay.

	Flow m^3 s^{-1}	Effluent discharge[a]		NH_4 at SRWTP µmol L^{-1}	*Realized loading* to Suisun Bay mmol m^{-2} d^{-1}	NH_4 at Suisun Bay (DWR-D4) µmol L^{-1}
		10^6 mol N d^{-1}	Tons N d^{-1}			
2009	345 ± 37	1.11 ± 0.26	15.54	37.62 ± 9.67	1.63	9.41
2010	518 ± 80	1.03 ± 0.10	14.42	23.38 ± 4.10	1.51	5.85

[a] Calculated from daily data from SRWTP.

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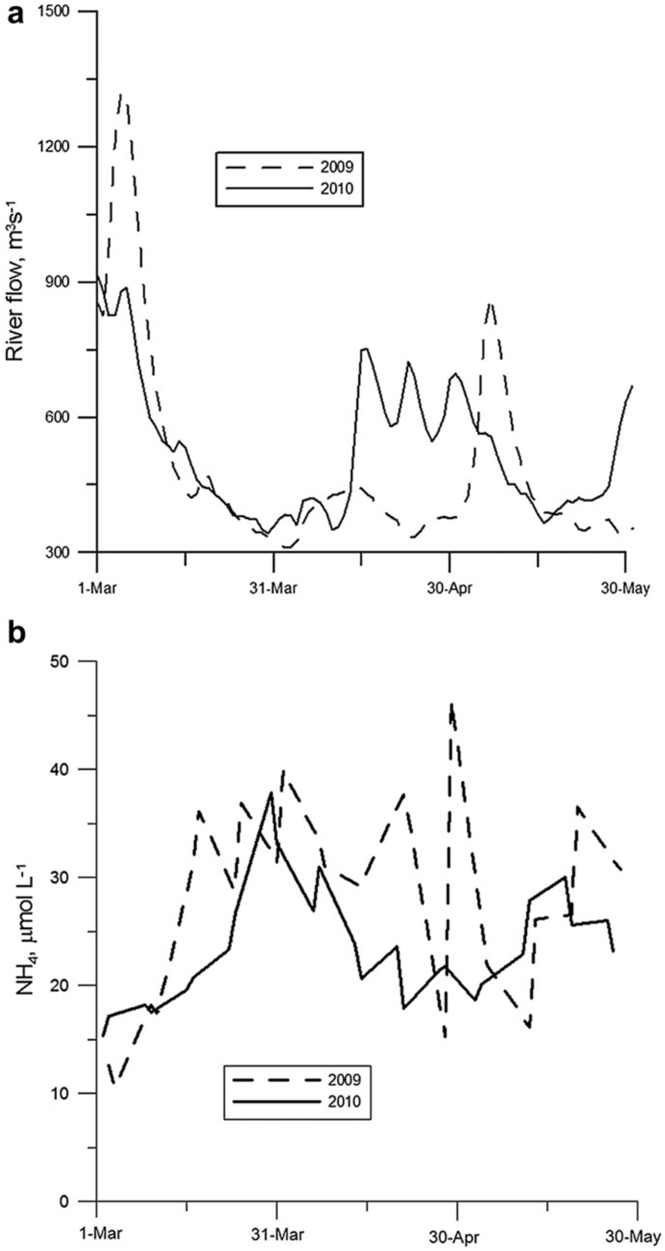

Fig. 7. Comparison of 2009 (dashed line) and 2010 (solid line) at SRWTP of a) River flow and b) NH_4 concentration calculated from the daily effluent NH_4 discharge and river flow.

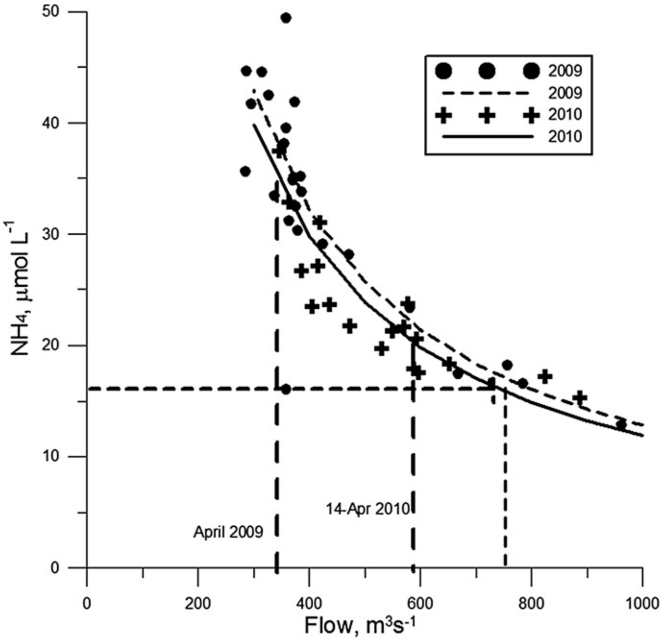

Fig. 8. Calculated concentration of NH_4 during March to May of 2009 (circles) and 2010 (crosses) at SRWTP versus river flow. Two hyperbolae were calculated using the average SRWTP discharge for April 2009 and 2010 (Table 3). The horizontal dashed line at 16 µmol L^{-1} corresponds to the 4 µmol L^{-1} Concentration Criterion realized at Suisun Bay. The vertical dashed lines designate mean April flow in 2009 and on 14 April 2010. The dotted vertical line shows the flow necessary to meet the Concentration Criterion at mean discharge for April 2010.

Flow rates were below the current Washout Criterion, 1100 $m^3\ s^{-1}$, during the 2010 study period (Fig. 7a) and the same was true for the spring period in 2009 except for early March (Fig. 7a). The interaction between calculated NH_4 concentration, discharge and flow can be visualized using the data for 2009 and 2010 (Fig. 8). The two hyperbolae were calculated for the mean April 2009 and 2010 estimates of discharge at SRWTP (Table 3). The NH_4 concentrations at SRWTP calculated from the daily discharge and flow data are shown. Some of the data for 2010 (crosses) falls below the hyperbola drawn through the mean conditions, indicating that during the study period in April 2010 discharge was reduced below the average value. The horizontal dotted line drawn from the *y*-axis at 16 µmol L^{-1} is the NH_4 concentration at SRWTP required to meet the Concentration Criterion at the entrance to Suisun Bay. The vertical dotted line indicates the flow (~760 $m^3\ s^{-1}$) required to reduce the concentration of NH_4 to 16 µmol L^{-1} at the discharge point and to 4 µmol L^{-1} at DWR-D4 in Suisun Bay. The left-most vertical dashed line drawn at average river flow for April 2009 (345 $m^3\ s^{-1}$) intersects the 2009 hyperbola at about 38 µmol L^{-1} (Table 3). The next vertical dashed line plotted for the river flow (592 $m^{-3}\ s^{-1}$) at SRWTP on 14 April 2010, intersects the 2010 hyperbola above the Concentration Criterion (dotted horizontal line). In 2009 the flow was too low to meet the Concentration Criterion whereas in 2010 the higher flow and the likely lower discharge allowed concentrations close to the criterion to be met.

5.5. Other factors that might influence the spring Suisun Bay blooms

Other possible factors that might influence bloom occurrences are improved irradiance, physical processes, e.g. entrapment or fronts, and changes in the clam population density. The irradiance field in the SFE is determined primarily by the sediment load, except for times of high chlorophyll concentrations, when the latter will also decrease the water column transparency. The sediment load has decreased substantially in the northern SFE, and is predicted to continue to decline, leading to improved irradiance conditions (McKee et al., 2006; Jassby, 2008; Schoellhamer, 2009). However, increased irradiance does not always result in phytoplankton blooms (Ball and Arthur, 1979). From 1999 to 2002, Suisun Bay had a mean Secchi depth of 0.3 m in spring (Wilkerson et al., 2006). In 2010 Secchi depths were greater and averaged 0.7 m prior to the bloom (Table 2). Depth-integrated NH_4 uptake rates were likely enhanced by the resultant deeper euphotic zone depth and this may have enabled the phytoplankton to meet the Loading Criterion.

Physical processes in addition to flow, which affects NH_4 concentration and interacts with growth rate to determine the threshold flow for washout, will also play a role in bloom initiation. Mixing often results in a homogeneous water column in Suisun Bay. Transient water column stratification may act to not only improve the average water column irradiance conditions but also may concentrate the phytoplankton and aid bloom formation. Such increased biomass would result in an increase in NH_4 uptake, another mechanism that would contribute to assimilation of the NH_4 load. One candidate for such a mechanism is the particle entrapment zone or turbidity maximum, a feature of many estuaries. In the SFE, a salinity of 2 has been shown to coincide with the turbidity maximum and the distance from the Golden Gate where the bottom water salinity declines to 2 and is referred to as X2 (Kimmerer, 2002). X2 was within Suisun Bay during the historic bloom periods observed by Ball and Arthur (1979) for a range of river flows and also in this study (X2 ~68 km, water.ca.gov/dayflow). The 2010 data set described here was obtained from surface samples only and not useful for investigating vertical distributions of water properties. However Fig. 4a shows that the blooms occurred in surface water of ≤ 2 suggesting that particle entrapment might have contributed to the bloom. A detailed study of the vertical salinity field during an ongoing bloom with nutrient and carbon uptake rate measurements is needed to better constrain the role of circulation and stratification in bloom development. Stratification would also create a barrier to benthic grazing on the phytoplankton.

The invasive clam, *Potamocorbula amurensis* (=*Corbula amurensis*) has been present in Suisun Bay since 1987 and considered the cause of the rapid decline in summer phytoplankton that occurred shortly after its introduction (Alpine and Cloern, 1992; Jassby et al., 2002). The clam population follows a seasonal cycle of growth and predation, with a biomass minimum in spring and biomass maximum in fall (e.g. Greene et al., 2011). The question arises; was the population lower in spring 2010 than 2009? In Suisun Bay similar population sizes were reported for spring 2009 and 2010, except for at DWR-D6 where the mean population of *P. amurensis* was higher in April 2010 (6337 ± 1226 individuals m^{-2}) than April 2009 (5985 ± 705 individuals m^{-2}) (Fuller, Bay-Delta Monitoring and Analysis, California Department of Water Resources, pers. comm.). The similarity in clam abundance between years argues against reduced grazing on phytoplankton in 2010 as a cause for the bloom.

In summary, the major drivers of the spring 2010 bloom in Suisun Bay were increased river flow and decreased discharge of NH_4 at SRWTP, enabling the phytoplankton population to absorb the inflowing NH_4 and reduce the NH_4 concentration to levels that would allow use of NO_3. The populations that arose were very similar quantitatively and qualitatively (diatom dominated) to pre-1987 Suisun blooms of phytoplankton.

5.6. *Food web response*

The cause(s) of the decline in pelagic fisheries in the northern SFE has so far eluded the scientific and management community. No sustained resurgence in fish populations has occurred in spite of extensive financial contributions towards habitat restoration and research (Sommer et al., 2007). The present study, in concert with other studies conducted in the northern SFE (Glibert et al., 2011; Parker et al., 2012c) suggests increased discharge of NH_4 into the Sacramento River as a cause of reduced phytoplankton blooms and the subsequent food-limited conditions in Suisun Bay. When this NH_4 discharge is reduced, the food web should respond positively. In May 2010, accompanying the observed phytoplankton blooms and lower NH_4 loading, there was a nine-fold higher abundance of the zooplankton food source (calanoid copepod adults) for the pelagic fishes in Suisun Bay compared to May 2009 (Hennessey, CA Dept. Fish and Game, pers. comm.), likely a result of the 2010 phytoplankton blooms described here. *Eurytemora affinis* increased from 32 individuals m^{-3} in May 2009 to 246 individuals m^{-3} in May 2010 and *Sinocalanus doerri* from 70 individuals m^{-3} in May 2009 to 1299 individuals m^{-3} in May 2010. Results from the 2010 Fall Midwinter Trawl Index for delta smelt and longfin smelt were 70% and 194% greater than those reported for 2009 (CA Dept. Fish and Game, dfg.ca.gov/delta/data/fmwt/charts.asp).

5.7. *Future predictions*

In December 2010, changes were approved to the SRWTP discharge permit requiring reductions in NH_4 inputs to the Sacramento River both through nitrification and denitrification. Reductions in NH_4 loadings should result in an increased probability of spring diatom blooms. Upgrading the SRWTP to full biological nitrogen removal (BNR, coupled nitrification/denitrification) would likely result in the Sacramento River phytoplankton productivity and community structure being driven by the conditions in the upper Sacramento River above the SRWTP (Parker et al., 2012c). These conditions of high NO_3, low NH_4 would likely fuel diatom blooms in Suisun Bay if the washout flow was not exceeded (i.e. the Washout Criterion) since both the Loading and Concentration Criteria would be met.

Increased irradiance conditions due to the expected decrease in sediment load (Schoellhamer, 2009) should result in an improved capacity of the phytoplankton to assimilate the NH_4 load to Suisun Bay from the Sacramento River, thereby reducing NH_4 concentrations to below NO_3 threshold, and enabling phytoplankton NO_3 use and blooms. The similarity in spring conditions occurring during the 2010 bloom (low NH_4, high chlorophyll, diatom success) with spring conditions (high chlorophyll and diatom dominance) that were described by Ball and Arthur (1979) for Suisun Bay from 1969 to 1979 suggests that a reversion to a diatom-fueled food web should also result in a return to the pre-1979 food web that supported larger zooplankton and higher food quality for fish. Ball and Arthur (1979) give mean values of chlorophyll of 30–40 $\mu g\ L^{-1}$ for Suisun Bay in spring and 40–100 $\mu g\ L^{-1}$ in summer 1969–1979 and according to Cloern and Cheng (1981) mean NH_4 concentrations for this period were low, in summer 1.8 and 4.0 $\mu mol\ L^{-1}$ in winter. These results suggest that the high concentrations of chlorophyll characteristic of the pre-1987 period could occur in spring if low NH_4 conditions were restored to the river and flow conditions were within prescribed limits. Phytoplankton could be restored to high spring chlorophyll conditions in Suisun Bay and even to high summer values if the clams were to disappear, as has happened elsewhere when NH_4 inputs were reduced (see case studies in Glibert, 2010). In this scenario, an increase in SFE productivity would follow the pattern of recovery observed in the Scheldt Estuary where nutrient inputs were reduced (Cox et al., 2009; Mialet et al., 2011). The present study provides an example of how the reduction of anthropogenic NH_4 inputs may be employed to restore pre-existing productivity to SFE and similarly impacted estuaries and coasts.

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

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ABSTRACT

Increased discharge of ammonium (NH_4) to the San Francisco Estuary (SFE), largely in treated domestic sewage effluent, has been linked to chronically food-limited conditions and to reduced fish abundance. Elevated chlorophyll concentrations at phytoplankton bloom levels are rarely observed if the ambient NH_4 concentrations are above 4 μmol L^{-1}—the NH_4 paradox. In both field samples and water held in enclosures for one week, an inverse relation was observed between NH_4 concentrations and nitrate (NO_3) uptake by phytoplankton, likely a result of inhibition of NO_3 uptake by NH_4. A simple model was constructed to examine the interaction between NH_4 and NO_3 inputs to the estuary, with varying freshwater river flow (hereafter termed flow) conditions. Sensitivity analyses were made and initial model parameters taken from an existing oceanic biogeochemistry model. Experiments were made with the model, and showed that initial NH_4 concentrations largely controlled the length of time to peak NO_3 uptake and NO_3 exhaustion. The model parameters were then tuned using observations from a set of enclosure experiments, and validated with results from a series of independent enclosure experiments with a variety of initial conditions. The model was run in three flow modes: (1) with no (zero) flow, (2) with flow, a fully mixed water column and a uniform light field, and (3) with flow, a fully mixed water column but with light attenuation and depth integrated values of N uptake. In the zero flow mode the model simulated enclosure experiments and when compared with enclosure results indicated the basic NH_4–NO_3 interactions to be correctly represented in the model. In the modes with flow, the model simulations reproduced a sharp transition from high phytoplankton productivity using both NO_3 and NH_4 to low productivity using only NH_4, simulating the historical effects of increasing NH_4 inputs to the SFE. With vertical integration to incorporate effects of irradiance, sharp boundaries at specific combinations of varying flow and NH_4 inputs were observed. The model could be embedded into three dimensional models of the SFE/Delta currently being implemented for management purposes such as regulating estuarine nutrients as required by the State of California and evaluating the effects of water management decisions on salmon and protected species of fish.

1. Introduction

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

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

Before 1980, Suisun Bay was characterized as a high chlorophyll ecosystem dominated by diatoms and large zooplankton (Ball and Arthur, 1979); it is now dominated by small phytoplankton,

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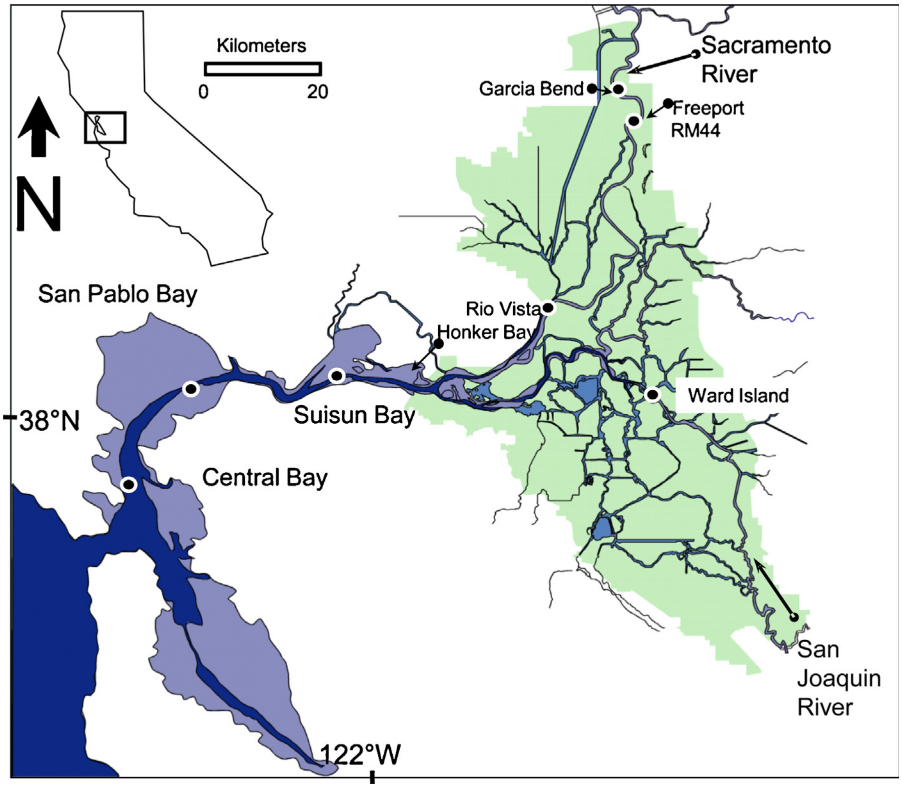

Fig. 1. Map of San Francisco Estuary/Delta California showing Suisun, San Pablo and Central Bays, and sampling locations along the Sacramento and San Joaquin rivers.

small zooplankton (Glibert et al., 2011) and low primary production (Kimmerer et al., 2012). High summer chlorophyll concentrations in Suisun Bay declined to low levels in 1987. Additionally spring blooms were not observed in Suisun Bay (Dugdale et al., 2012). The invasive Asian overbite clam (*Potamocorbula amurensis*) appeared in substantial numbers at that time and is considered the primary reason for the crash in phytoplankton biomass (Alpine and Cloern, 1992). However clam populations are low in spring (Greene et al., 2011) and grazing is insufficient to explain the lack of spring blooms. Nutrients had been neglected as a factor in regulation of primary production in the SFE as N, Si and P were all in excess of requirements throughout the year (Jassby et al., 2002). However, the decline in chlorophyll in Suisun Bay (in all seasons) began at about the same time as NH_4 discharge and concentrations began to increase rapidly in the Sacramento River the main water source for Suisun Bay (Glibert et al., 2011), the result of both increases in urban populations and agricultural use of nitrogen fertilizers (Jassby, 2008). In 1984 there were 5.2 tons NH_4-N day^{-1} added to the Sacramento River at Freeport from municipal waste (Schemel and Hager, 1986); additional natural/agricultural NH_4 in the Sacramento River was less than or equal to half of the effluent input. Today, discharge of NH_4 at Freeport is about 15 tons NH_4-N per day (Jassby, 2008).

A growing body of evidence points to NH_4 inputs of anthropogenic origin as a driving factor in the decline and eventual collapse of the primary productivity of the northern SFE and in particular of Suisun Bay (e.g. Dugdale et al., 2007; Glibert et al., 2011; Dugdale et al., 2012). Measurements of dissolved inorganic N (DIN) uptake by phytoplankton using incubations with $^{15}NO_3$ and $^{15}NH_4$ as tracers have indicated that nutrients in SFE are important in determining phytoplankton productivity (Wilkerson et al., 2006; Dugdale et al., 2007, 2012; Parker et al., 2012a,b). NO_3 is rarely used in the SFE/Delta as a consequence of suppression of NO_3 uptake by NH_4, with phytoplankton blooms occurring in the SFE only when NH_4 concentrations declined to low levels (Wilkerson et al., 2006; Dugdale et al., 2007). NO_3 uptake is essential for high productivity rates and phytoplankton bloom occurrence as NO_3 is the largest reservoir of DIN in the SFE (Wilkerson et al., 2006; Dugdale et al., 2012). Decreased phytoplankton growth rates and reduced carbon fixation (primary production) occurred when the algae were using NH_4 compared to NO_3 (Wilkerson et al., 2006; Parker et al., 2012a). When chlorophyll concentrations and NO_3 uptake rates were plotted against NH_4 concentration, a threshold of about 4 μmol L^{-1} NH_4 appeared to delineate the level at which suppression of NO_3 uptake occurred. Below this concentration, NO_3 uptake was enabled and occurred even more rapidly when NH_4 concentrations decreased to ~1 μmol L^{-1} accompanied by a rapid increase in chlorophyll (Dugdale et al., 2007).

To understand the sequence of events involved in the NH_4 response by phytoplankton, to use in simulation models, experiments were made with water from Central San Francisco Bay that was enclosed and incubated under natural light. The phytoplankton response in the enclosed water followed the pattern shown in Fig. 2 (taken from Dugdale et al., 2007) that has been repeatedly observed (e.g. Parker et al., 2012a). First NH_4 concentrations decreased and then NO_3 concentrations decreased rapidly to zero within four days (Fig. 2a and b) (Dugdale et al., 2007). During this four day cycle, the biomass-specific NO_3 uptake rate (VNO_3) increased to a peak at Day 2 or 3 and then declined rapidly as NO_3 was depleted (Fig. 2c). The biomass-specific NH_4 uptake rate (VNH_4) remained relatively unchanged or decreased (Fig. 2d). Chlorophyll accumulation (Fig. 2e) occurred as NO_3 was drawn down. This rapid use of NO_3 observed in SFE water is virtually identical to that observed in newly upwelled ocean water (Wilkerson and Dugdale, 1987; Dugdale et al., 2006) and incorporated into a productivity model that included acceleration or “shift up” of NO_3 uptake rates (Dugdale et al., 1990). The essential feature of this shift-up model is that the biomass specific NO_3 uptake rate, VNO_3 (equivalent to a nitrogen-based growth rate) increases at a rate proportional to the ambient NO_3 concentration. Since NO_3 is usually

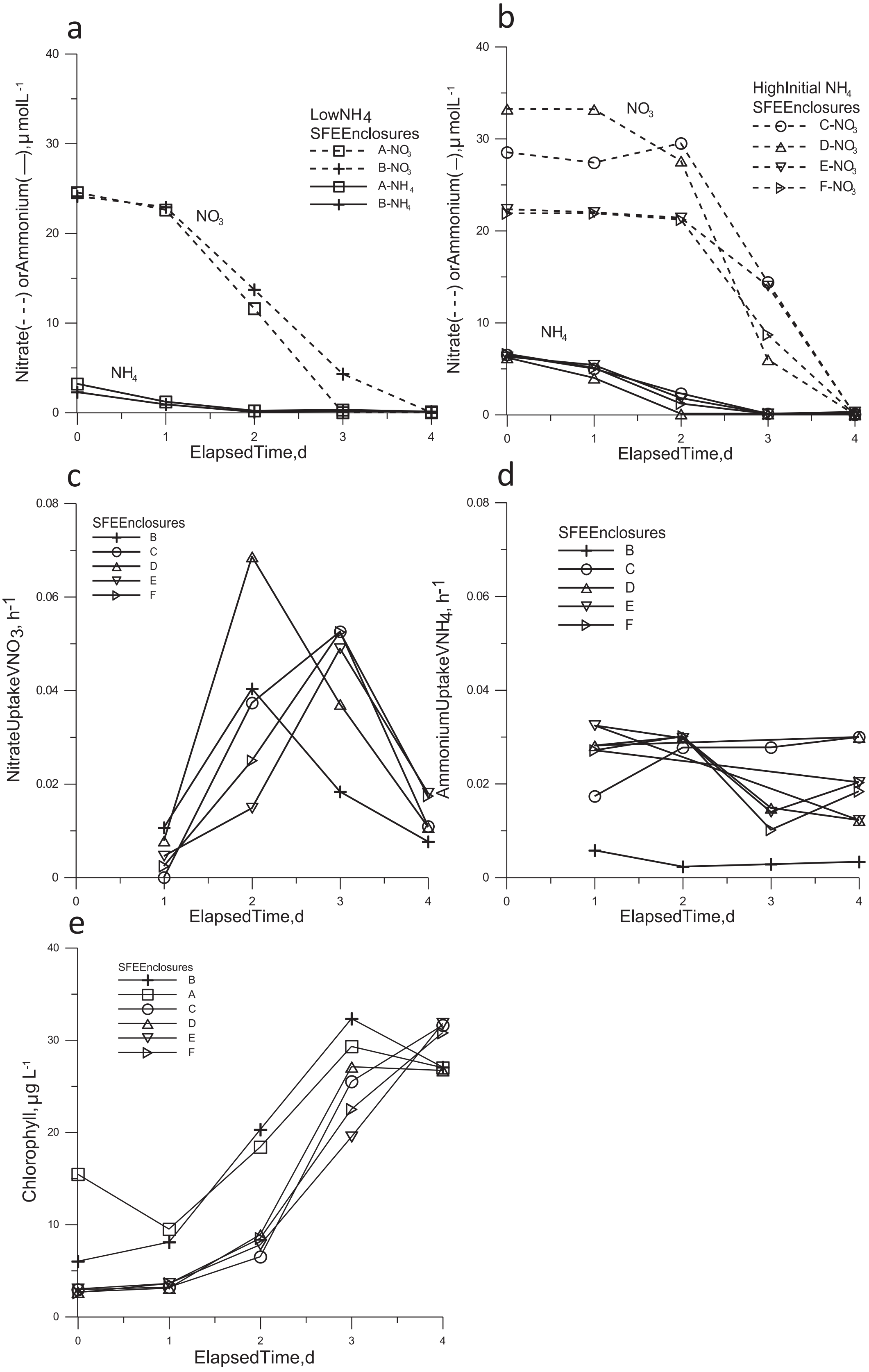

Fig. 2. Time course in enclosures filled with Central Bay water of (a) NO_3 and NH_4 concentrations in enclosures with low initial NH_4 (Enclosures A and B); (b) NO_3 and NH_4 concentrations in enclosures with high initial NH_4 (Enclosures C, D, E, F); (c) specific uptake rates of NO_3, (d) specific uptake rates of NH_4; (e) chlorophyll concentration (from Dugdale et al., 2007).

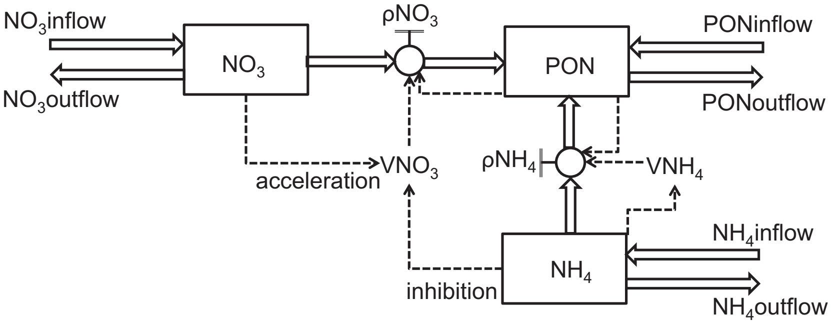

Fig. 3. Diagram of the biogeochemical model showing flows of NH_4, NO_3 and PON (thick arrows) and control processes in dotted lines including acceleration of VNO_3 by NO_3 and inhibition of VNO_3 by NH_4.

the largest DIN pool in the SFE this will lead to enhanced growth when it is used compared to NH_4, that is typically the smaller pool of DIN. The effect can be seen in the VNO_3 vs. elapsed time curve for enclosure D (Fig. 2c) which has the steepest slope and is the enclosure with the highest initial NO_3 concentration (Fig. 2b). Consequently, VNO_3 increases with time until NO_3 concentration falls to the Michaelis-Menten limiting range for uptake. This accounts for the result, that all NO_3 is exhausted by the phytoplankton in the same length of time, about 4 days, regardless of the initial ambient NO_3 (Fig. 2a and b).

In the northern SFE rare spring blooms are enabled by access to the NO_3 pool accompanied by high productivity rates when NH_4 concentrations are low (Wilkerson et al., 2006; Dugdale et al., 2012). In the period 2000–2010, in Suisun Bay, only two phytoplankton blooms were observed in Suisun Bay: the first in 2000 (Wilkerson et al., 2006) and a second in 2010 (Dugdale et al., 2012). Both blooms (>30 $\mu g\,L^{-1}$ chlorophyll) occurred when NH_4 concentrations were about 1 $\mu mol\,L^{-1}$ (Dugdale et al., 2012). Dugdale et al. (2012) developed a conceptual model for the prediction of blooms in Suisun Bay with three required criteria (NH_4 loading criterion, NH_4 concentration criterion and a washout river flow criterion). This analysis highlighted the combined importance of freshwater (river) flow and NH_4 concentration in determining bloom initiation in the northern SFE.

A more complete understanding of the role of anthropogenic NH_4 and flow in modulating productivity in the SFE will require the development of linked biogeochemical and hydrodynamic models. Here, we evaluate potential productivity of Suisun Bay using a simple biogeochemical model. The model is based on results from field and enclosure experiments conducted in the northern SFE and constructed to be run in a three modes: (1) with no (zero) flow, (2) with flow, a fully mixed water column and a uniform light field, and (3) with flow, a fully mixed water column but with light attenuation and depth integrated values of N uptake. From resulting model runs we make predictions for the potential effects of managed perturbations in the Suisun Bay ecosystem, e.g. reduction in allowable discharge of anthropogenic NH_4 in sewage effluent and/or changes in freshwater flow.

2. Model development and construction

Our strategy was to construct a biogeochemical simulation model, linking NH_4 and NO_3 inputs, phytoplankton uptake, and freshwater flow, make initial runs with zero flow (mode 1) to compare with data collected using enclosure experiments, and then tune the model as necessary to reproduce the observed effect of NH_4 on NO_3 uptake. The model was tested (without flow) against an independent data set from enclosure experiments. Finally the model was run with added freshwater flow effects (modes 2 and 3). The model was constructed and run using Stella 10.0 (Ieesystems.com). The flows and controls are shown in Fig. 3 and the parameters listed in Table 1 with the values used for different model runs in Table 2. The currency of the model is nitrogen and the pools are NO_3, NH_4, and particulate nitrogen (PON). Inflows and outflows are allowed for all three pools. In constructing this model, we drew upon our previous work in developing a biogeochemical ecosystem model — the CoSiNE (Carbon, Silicate, Nitrogen Ecosystem) model (Chai et al., 2002; Dugdale et al., 2002) that has been incorporated into Pacific basin-wide and coastal ROMS models (e.g. Xiu and Chai, 2012), reproducing many important features of these ecosystems. The present model incorporates CoSiNE phytoplankton uptake kinetics (Michaelis-Menten formulation) and an exponential function (ψ) for NH_4 inhibition of NO_3 uptake (Chai et al., 2002).

The SFE biogeochemical model incorporates kinetic parameters from the CoSiNE model (Chai et al., 2002), appropriate for diatoms which are the major functional group that dominates the final population in enclosure experiments in SFE and in phytoplankton blooms in Suisun Bay (Parker et al., 2012a; Dugdale et al., 2012; Cloern and Dufford, 2005). Diatoms are fast-growing and outcompete other phytoplankton in high nutrient conditions, e.g. in coastal upwelling. They prefer, and under some conditions physiologically require NO_3 over NH_4 (Syrett, 1981; Berg et al., 2001; Glibert et al., 2006). The model incorporates the concept of shift up, i.e. acceleration of NO_3 uptake which is not included in the CoSiNE formulation. The formulation for the acceleration of NO_3 uptake (A) to calculate maximum specific NO_3 uptake is a function of NO_3 concentration as used in Dugdale et al. (1990). The model is run with a time step of

Table 1
List of model parameters and units.

Parameter	Unit
Flow	$m^3\,s^{-1}$
$NH_4(t)$	$\mu mol\,L^{-1}$
NH_4 inflow	$\mu mol\,L^{-1}\,h^{-1}$
NH_4 outflow	$\mu mol\,L^{-1}\,h^{-1}$
ρNH_4	$\mu mol\,L^{-1}\,h^{-1}$
VNH_4	h^{-1}
$NO_3(t)$	$\mu mol\,L^{-1}$
NO_3 inflow	$\mu mol\,L^{-1}\,h^{-1}$
NO_3 outflow	$\mu mol\,L^{-1}\,h^{-1}$
ρNO_3	$\mu mol\,L^{-1}\,h^{-1}$
VNO_3	h^{-1}
$PON(t)$	$\mu mol\,L^{-1}$
PON inflow	$\mu mol\,L^{-1}\,h^{-1}$
PON outflow	$\mu mol\,L^{-1}\,h^{-1}$
$V_{max}NH_4$	h^{-1}
K_SNH_4	$\mu mol\,L^{-1}$
K_SNO_3	$\mu mol\,L^{-1}$
α	h^{-2}
β	h^{-2}
ψ	dimensionless

Table 2
Values used for model parameters in different runs; parameters kept constant in all runs were initial $VNO_3 = 0.03\,h^{-1}$, $\beta = 4 \times 10^{-5}$, $\psi = -5.59$, $K_SNH_4 = 1\,\mu mol\,L^{-1}$, $K_SNO_3 = 1\,\mu mol\,L^{-1}$.

Figure #	Enclosure Exp.	$NH_4(i)$ ($\mu mol\,L^{-1}$)	$NO_3(i)$ ($\mu mol\,L^{-1}$)	PON(i) ($\mu mol\,L^{-1}$)	α ($\times 10^{-5}\,h^{-2}$)	A (h^{-2})
4		6.0	30.0	3.0	4	0.00124
4		6.0	20.0	3.0	4	0.00084
5		2.0	30.0	3.0	4	0.00124
5		2.0	20.0	3.0	4	0.00084
7	Enclosure A	2.3	24.1	7.2	8	0.00197
7	Enclosure C	6.5	28.5	3.4	8	0.00232
7	Enclosure E	6.3	22.3	3.6	8	0.00182
8-XB2002	Control	6.8	18.7	4.5	8	0.00153
8-XB2002	$+5NH_4$	12.4	18.7	4.5	8	0.00153
8-XB2002	$+10NH_4$	17.9	18.7	4.5	8	0.00153
8-XB2002	$+20NH_4$	26.0	18.7	4.5	8	0.00153
8-XB2002	$+30NH_4$	36.0	18.7	4.5	8	0.00153
9-WB09-1	Garcia Bend	1.0	13.1	3.0	8	0.00109
9-WB09-1	Garcia + NH_4	12.4	13.3	3.6	8	0.00111
9-WB09-1	Garcia + NO_3	1.5	24.6	4.0	8	0.00201
9-WB09-1	RM44	12.4	13.3	3.6	8	0.00111
10-Bad Suisun 3	Central Bay	7.6	24.1	6.7	8	0.00124
10-Bad Suisun 3	Suisun Bay	3.8	43.7	6.8	8	0.00354
10-Bad Suisun 3	Rio Vista	9.0	19.2	3.1	8	0.00158
10-Bad Suisun3	San Joaquin	5.1	26.2	3.7	8	0.00124
11 Fixed flow	Variable NH_4	0.1–10.0	30.0	3.0	4	0.00124
12-Variable flow	Integrated mode	5.0 and 10.0	30.0	6.8	4	0.00124
13-Variable flow	variable NH_4, integrated mode	1.0–10.0	30.0	3.0	8	0.00244

one hour, consistent with the units reported for the kinetic parameters for N uptake. The model is stable at this time step and no gain in precision is likely to be achieved by using smaller time steps. To evaluate daily rates, since NO_3 uptake occurs over 12 h and NH_4 uptake over 18 h (Wilkerson et al., 2000) each hourly rate is multiplied by 0.5 for NO_3 uptake and by 0.75 for NH_4.

Equations governing the model are:

To determine NH_4 balance in an embayment:

$$NH_4(t) = NH_4(t - dt) + (NH_4\,\text{inflow} - \rho NH_4 - NH_4\,\text{outflow}) \times dt \tag{1}$$

where $NH_4(t)$ is NH_4 after time, t; dt is the time interval (1 h) and

$$NH_4\,\text{inflow} = NH_4(i) \times \text{flow} \tag{2}$$

and

$$\rho NH_4 = VNH_4 \times PON \times 0.75 \tag{3}$$

where VNH_4 is biomass specific uptake rate (h^{-1}) and PON is particulate organic nitrogen concentration (i.e. phytoplankton biomass) and $NH_4(i)$ is initial NH_4 concentration.

$$NH_4\,\text{outflow} = NH_4 \times \text{flow} \tag{4}$$

To determine NO_3 balance:

$$NO_3(t) = NO_3(t - dt) + (NO_3\,\text{inflow} - \rho NO_3 - NO_3\,\text{outflow}) \times dt \tag{5}$$

$$NO_3\,\text{inflow} = NO_3(i) \times \text{flow} \tag{6}$$

$$\rho NO_3 = VNO_3 \times PON \times 0.5 \tag{7}$$

$$NO_3\,\text{outflow} = NO_3 \times \text{flow} \tag{8}$$

To determine PON balance:

$$PON(t) = PON(t - dt) + (\rho NO_3 + \rho NH_4 + PON\,\text{inflow} - PON\,\text{outflow}) \times dt \tag{9}$$

$$PON\,\text{inflow} = PON(i) \times \text{flow} \tag{10}$$

$$PON\,\text{outflow} = PON \times \text{flow} \tag{11}$$

To determine phytoplankton uptake rates

$$VNH_4 = V_{\max}NH_4 \times \frac{NH_4}{NH_4 + K_SNH_4} \tag{12}$$

$$VNO_3 = (VNO_3(i) + A \times t) \times \frac{NO_3}{K_SNO_3 + NO_3} \times \exp^{(-y \times NH_4)} \tag{13}$$

$$A = \alpha \times NO_3 + \beta \tag{14}$$

where A is acceleration of uptake, K_SNH_4 and K_SNO_3 are half saturation constants, Ψ is a constant for NH_4 inhibition of NO_3 uptake.

The equations unique to this model are the inhibition of NO_3 uptake by NH_4, by an exponential effect with parameter Ψ and the increase of maximal NO_3 uptake with time by the acceleration term A. The term A has two elements, α which is multiplied by the ambient NO_3 concentration, and a constant β (Dugdale et al., 1990); both have units of t^{-2}. α is the more important element. For example, with $NO_3 = 30\,\mu mol\,L^{-1}$, elapsed time of 240 h, and $\alpha = 4 \times 10^{-5}\,h^{-2}$, an increase of VNO_3 of $0.29\,h^{-1}$ results while $\beta \times t$ for the same period results in an increase of only $0.01\,h^{-1}$, about 3% of the increase due to α. Parameters used in each model run and associated with each figure are provided in Table 2. For the initial model runs to simulate enclosures, the values of Ψ were taken from Chai et al. (2002). Data supplied to the model are initial concentrations of NH_4, NO_3 and PON and in modes 2 and 3, freshwater flow.

3. Model runs with zero flow

3.1. Model run with zero flow, variable initial NO_3, high initial NH_4 concentration

The way the model works is illustrated in Fig. 4, the results of model runs at two initial NO_3 concentrations (20 or 30 $\mu mol\,L^{-1}$) and initial NH_4 at 6 $\mu mol\,L^{-1}$. No change in NO_3 concentration

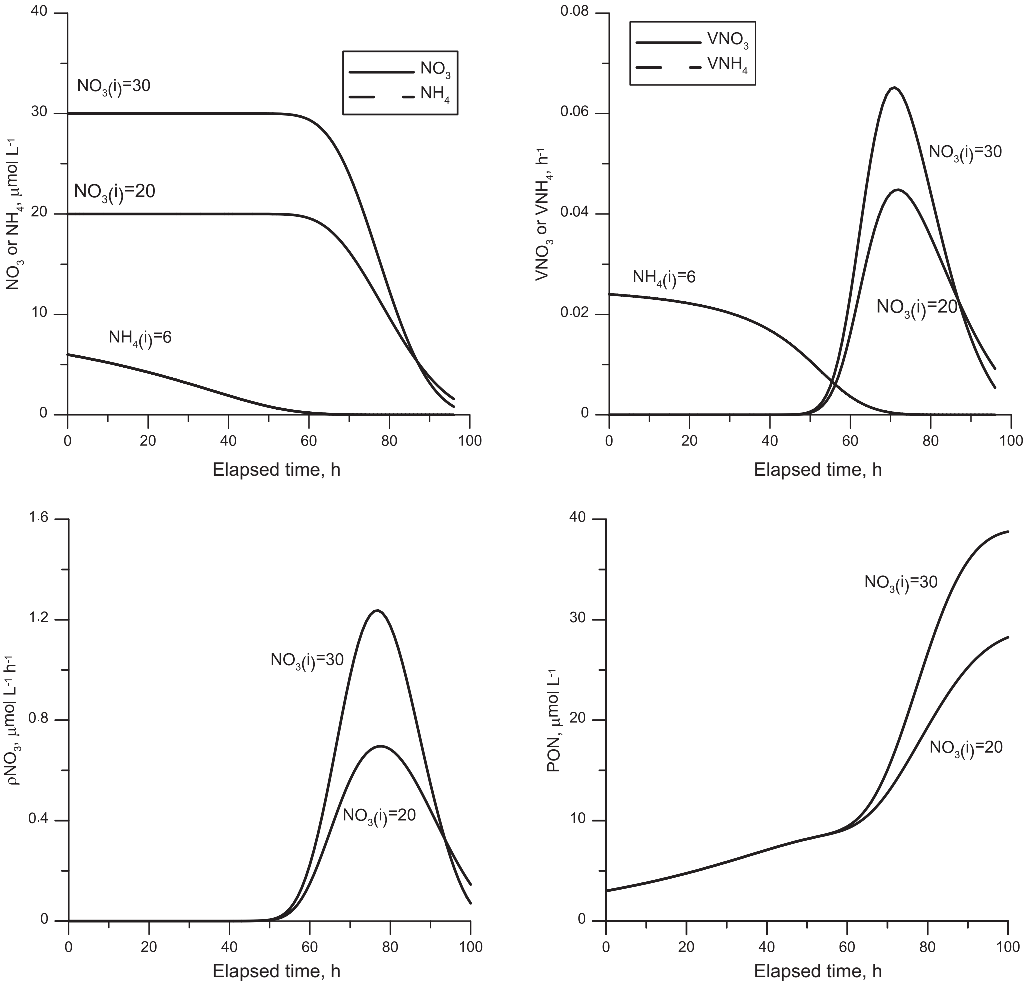

Fig. 4. Model with no flow and fixed high initial NH_4 concentration (6 µmol L^{-1}): the effects of varying NO_3 concentrations (20 or 30 µmol L^{-1}) on (a) concentration of NO_3 and NH_4; (b) specific uptake rates of NO_3 and NH_4; (c) uptake rate (ρ) of NO_3; (d) PON concentration versus elapsed time.

occurs until NH_4 concentration declines to low, non-inhibiting concentrations as a result of NH_4 uptake by the phytoplankton (Fig. 4a). The time to exhaust the initial NO_3 is the same for both conditions, 96 h, regardless of the initial NO_3 concentration, as previously described for the shift-up model (Dugdale et al., 1990). The processes leading to this result occur in a sequence. First, there is an increase in NO_3 uptake on a biomass basis (VNO_3) associated with increasing NO_3 concentration, which peaks at 72 h (Fig. 4b). This increase in uptake is a result of the acceleration term, A (Eqs. (13) and (14)) such that the initial slope of the VNO_3 vs. time curve is steeper for the higher NO_3 concentration. The peak VNO_3 (Fig. 4b) occurs as NO_3 concentrations decline (Fig. 4a), acceleration rates decrease and VNO_3 begins to decline (Fig. 4b). The peak VNO_3 is higher for the higher initial NO_3 concentration as a result of the higher initial acceleration rates. The timing of the VNO_3 peak, at about 72 h for both initial NO_3 concentrations is largely dependent on the shape of the NO_3 concentration versus time curve (Fig. 4a). For the first 60 h, biomass (PON) increases at a relatively low rate due to NH_4 uptake and then increases rapidly (Fig. 4d) as NO_3 uptake begins. The actual (transport) uptake rate ρNO_3 is the product of VNO_3 and PON concentration, (Eq. (7)). In the low NH_4 period VNO_3 is increasing and PON is also accumulating with the result that a rapid increase in ρNO_3 occurs (Fig. 4c). The peak in ρNO_3 (Fig. 4c; 79 h) occurs slightly later than the peak VNO_3 (Fig. 4b; 72 h) delayed due to the continuing accumulation of biomass as PON partially compensating for the decline in VNO_3. The final result is a more rapid increase in PON and a higher concentration of PON with the higher initial NO_3.

3.2. *Model run with zero flow, variable initial NO_3, low initial NH_4 concentration*

With lower initial NH_4 concentration (i.e. 2 µmol L^{-1}), and initial NO_3 of 20 or 30 µmol L^{-1}, NO_3 concentration (Fig. 5a) declines earlier than in the high NH_4 concentration runs (Fig. 4a). The time of NO_3 exhaustion (at 96 h) is virtually the same for the different initial NO_3 values, (Fig. 5a) and at high NH_4 initial concentrations (Fig. 4a). The peak values of VNO_3 are still a direct function of the initial NO_3 concentration (Fig. 5b), but the curves are broader with time and occur about 10 h earlier (at 62 h elapsed time) than with higher initial NH_4 concentration (Section 3.1, Fig. 4b). The NO_3 uptake (ρNO_3) curves (Fig. 5c) are broader in the low NH_4 runs. As in the high initial NH_4 runs, the uptake peaks of ρNO_3 (Fig. 5c) are delayed relative to VNO_3 (Fig. 5b), a result of the delay in accumulation of biomass as PON (Fig. 5d). As in the runs with high NH_4 concentration, these patterns are controlled largely by the rates of decline of NO_3, which starts earlier in the low NH_4 runs, but ends at the same time as the high NH_4 concentration runs, a consequence of the shift-up model

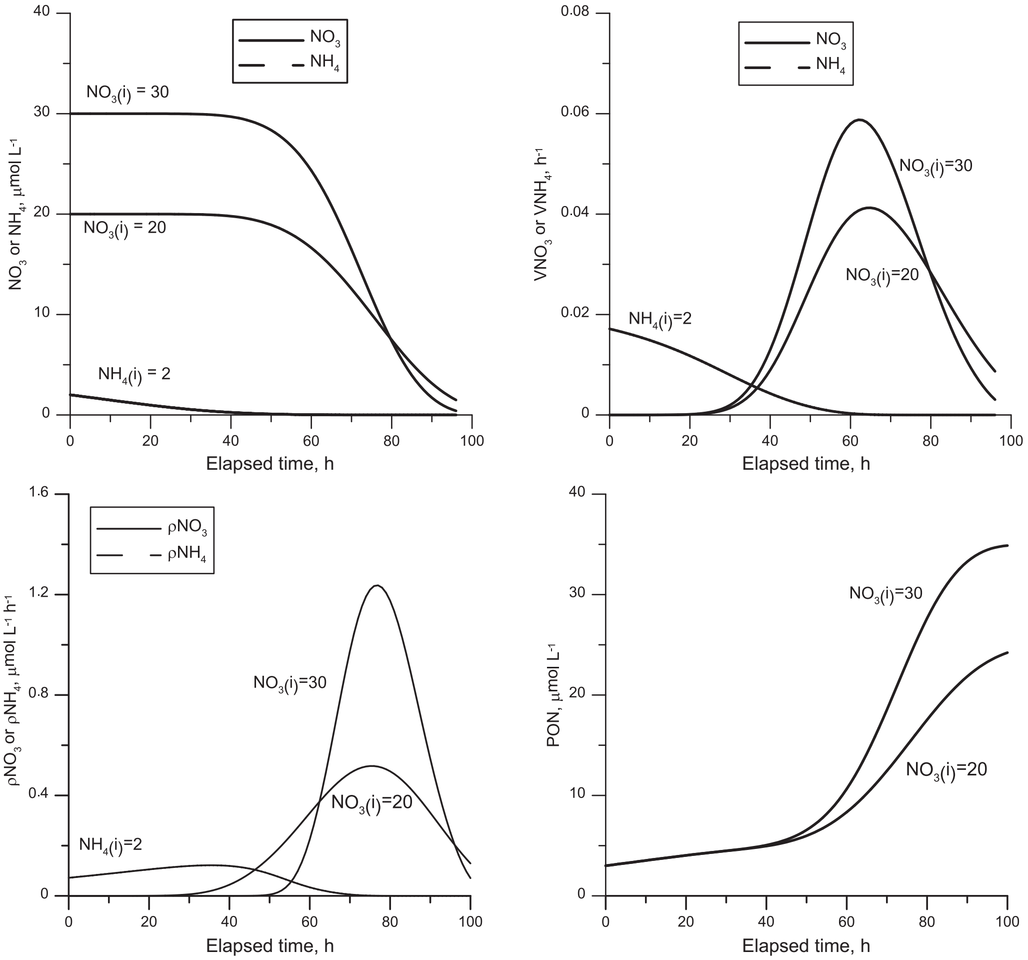

Fig. 5. Model with no flow and fixed low initial NH_4 concentration (2 μmol L^{-1}): the effects of varying NO_3 concentrations (20 or 30 μmol L^{-1}) on (a) concentration of NO_3 and NH_4; (b) specific uptake rates of NO_3 and NH_4; (c) uptake rate (ρ) of NO_3; (d) PON concentration versus elapsed time.

property of NO_3 exhaustion occurring at a relatively constant time regardless of the initial NO_3 concentration.

3.3. Sensitivity analysis

3.3.1. Effects of parameters on the time to NO_3 depletion to zero

The NH_4 uptake rate determines the elapsed time before NO_3 uptake occurs. The value of K_SNH_4 affects the rate of NH_4 uptake (Eq. (12)) and a sensitivity analysis was made of the influence of K_SNH_4 on the model output. The time to zero NO_3 appears as a linear function of K_SNH_4 (Fig. 6a) but the dependence of the time to NO_3 exhaustion was not very sensitive to the value of K_SNH_4, increasing the time to exhaustion by only 40 h, from 120 to 160 h. Diatoms are components of the ecosystem that are of the “r” type that compete on the basis of fast growth rates rather than on the ability to take up nutrients at low concentrations i.e. low K_S. High growth rates (V_{max}) are usually correlated with high K_S values. The effect of different initial NH_4 concentrations on the time to exhaustion was shown to be small in model runs (Figs. 4 and 5) so it would be expected that K_SNH_4 values also have little effect on time to exhaustion.

The effect of K_SNO_3 is small as it occurs only late, when NO_3 concentration drops rapidly (not shown). The time to NO_3 exhaustion is strongly dependent on the acceleration term, in particular the element α. With $\alpha = 0\ h^{-2}$, the time to NO_3 exhaustion is about 220 h, but drops to 110 h at $\alpha = 4 \times 10^{-5}\ h^{-2}$ with little changes at higher values (Fig. 6b). The value of ψ has little effect on the time for NO_3 exhaustion (Fig. 6c).

3.3.2. Effects of parameters on peak VNO_3 and time of peak VNO_3

The value of K_SNH_4 has little effect on the peak value of VNO_3 (Fig. 6d), but affects the time that peak VNO_3 is reached (Fig. 6d), from ~50 h at $K_SNH_4 = 0$ μmol L^{-1} to nearly 150 h at $K_SNH_4 = 3$ μmol L^{-1}, a 3-fold increase. The peak value of VNO_3 is a nearly linear function of α, increasing from 0.02 to 0.12 h^{-1} at $\alpha = 10 \times 10^{-5}\ h^{-2}$ (Fig. 6e). The time at which the peak value of VNO_3 is reached occurs at 180 h with $\alpha = 0\ h^{-2}$ and drops to 60 h at $\alpha = 1 \times 10^{-5}\ h^{-2}$; little change in VNO_3 occurs at higher α (Fig. 6e). The greatest effect of ψ on VNO_3 and time to peak VNO_3 is observed between $\psi = 0$ (no inhibition) to $\psi = -2$; above that value little change in VNO_3 occurs (Fig. 6f).

Responses to ±50% changes in parameters from the standard model run conditions are shown in Table 3. Changes in K_SNH_4 result in little change in time to NO_3 exhaustion or to peak VNO_3, but a −50% change in K_SNH_4 results in a −15% change in time of the peak VNO_3. The 50% perturbation of α results in a +20% and −10% change in time to NO_3 exhaustion, a −38% to +35% change in peak VNO_3, and a +10% to −3% change in time of peak VNO_3. The maximum response due to a 50% perturbation of ψ is a 4% reduction in peak VNO_3.

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

Trials of the model were first made using initial input parameters from a series of enclosure experiments (Enclosure A (experiment named 9901), Enclosure C (9903) and Enclosure E

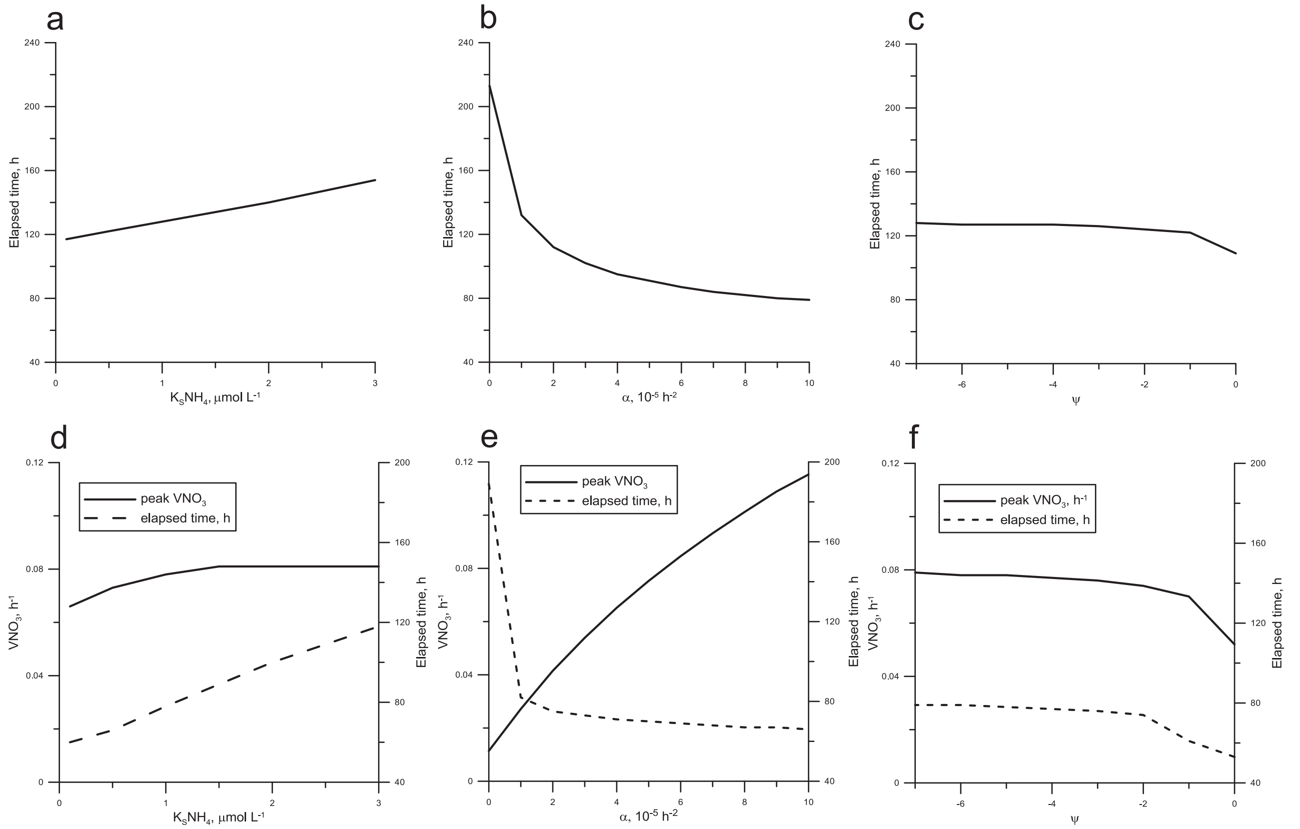

Fig. 6. Sensitivity analyses: the effect of (a) K$_S$NH$_4$; (b) α; (c) ψ. on the elapsed time taken for NO$_3$ to reach zero, and of (d) K$_S$NH$_4$; (e) α; (f) ψ on the peak value of VNO$_3$ and the elapsed time to reach peak VNO$_3$.

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

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

Table 3
Sensitivity analysis.

Parameter	%change from standard run	Time to NO$_3$ = 0 (h)	%change from standard run	Peak VNO$_3$ (h^{-1})	%change from standard run	Elapsed time at peak VNO$_3$ (h)	%change from standard run
K$_S$NH$_4$ (μmol L^{-1})							
1	100	128	0.0	0.078	0.0	78	0.0
0.5	−50	122	−4.7	0.073	−6.4	66	−15.4
1.5	50	134	4.7	0.081	3.9	89	14.1
α ($\times 10^{-5}$ h^{-2})							
4	100	128	0.0	0.078	0.0	78	0.0
2	−50	153	19.5	0.048	−38.5	85	9.0
6	50	115	−10.2	0.105	34.6	76	−2.6
ψ							
−5.59	100	128	0.0	0.078	0.0	78	0.0
−2.80	−50	126	−1. 6	0.075	−3.9	76	−2.6
−8.39	50	129	0.8	0.080	2.6	80	2.6

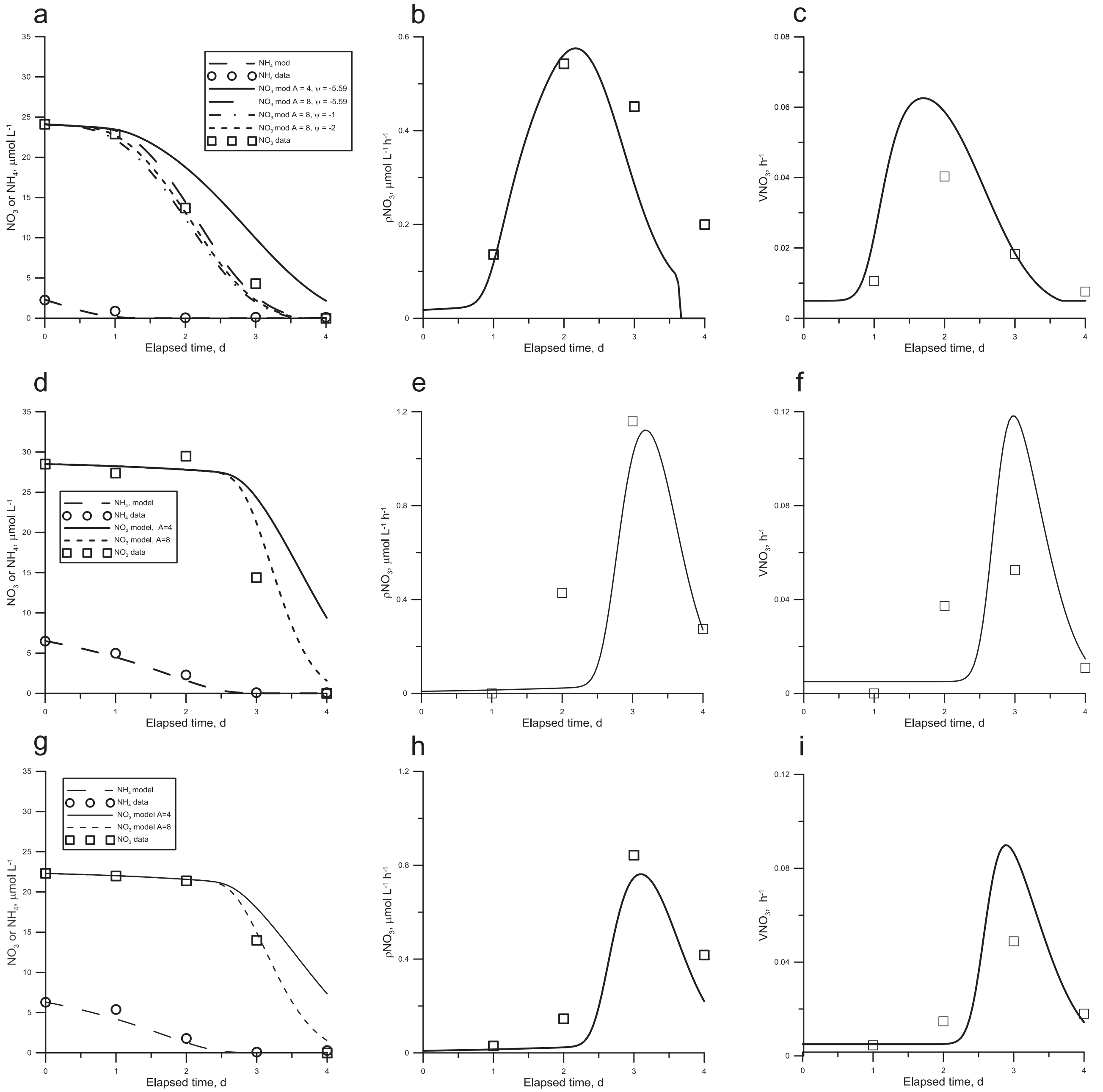

Fig. 7. Time course of modeled (lines) enclosure nutrient concentration (a, d, g), ρNO_3 uptake data (b, e, h) and VNO_3 (c, f, i) compared with observed enclosure data (symbols, □ for NO_3, ○ for NH_4) for three sets of enclosure experiments made using water from Central Bay (a–c, Enclosure A, d–f Enclosure C, g–i, Enclosure E) that had different initial conditions. (a) concentrations of NO_3 and NH_4 with $\alpha = 4 \times 10^{-5}$ h^{-2}, $\psi = -5.59$ (solid line); $\alpha = 8 \times 10^{-5}$ h^{-2}, $\psi = -5.59$ (dashed line); $A = 8 \times 10^{-5}$ h^{-2}, $\psi = -1$ (dash, dot line); $\alpha = 8 \times 10^{-5}$ h^{-2}, $\psi = -2$ (dotted line); (d, g) concentrations of NO_3 and NH_4 with $\alpha = 4 \times 10^{-5}$ h^{-2}, $\psi = -5.59$ (solid line); $\alpha = 8 \times 10^{-5}$ h^{-2}, $\psi = -5.59$ (dashed line).

variability in the observed data due to the presence of detrital-N in the PON pool being measured using mass spectrometry. However, the values of ρNO_3 are robust as any detrital particulate N that dilutes the VNO_3 is canceled by the higher PON (Dugdale and Wilkerson, 1986). The only parameter that was varied to obtain a fit of the model and Central Bay enclosure data concentration pattern with time was α in the calculation of acceleration, *A*.

3.5. *Model validation using independent data*

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

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

Manipulated enclosure experiments (XB2003) were made in which additions of NH_4 were made, at 5, 10, 20 and 30 µmol L^{-1} to water collected from Central Bay (Fig. 1) and the effects followed for four days (see Dugdale et al., 2007). Each enclosure was sampled daily for nutrient and chlorophyll concentrations, and $^{15}NH_4$ and $^{15}NO_3$ uptake incubations made with 50% ambient irradiance, cooled with flowing bay water.

The time course of modeled concentrations of NO_3 and NH_4, and uptake are plotted along with the data from the five enclosures in Fig. 8a–j. The modeled exhaustion point for NH_4 (i.e. to reach zero)

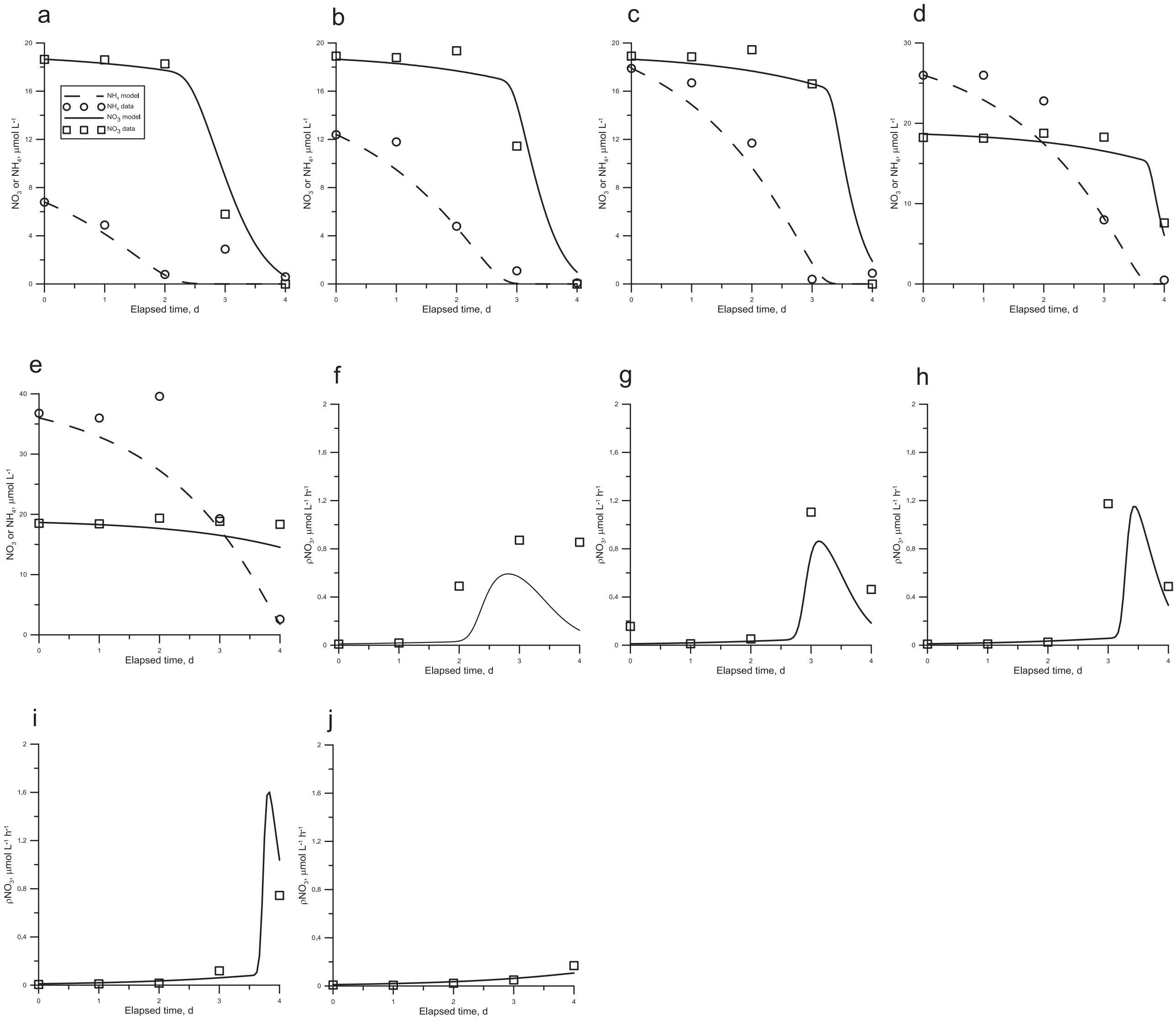

Fig. 8. Time course of modeled (solid line for NO_3, dashed line for NH_4) compared with observed (□ for NO_3, ○ for NH_4) enclosure data for enclosure experiments (XB2002) made using water from Central Bay amended with increasing NH_4 (0, 5, 10, 20, 30 μmol L^{-1}). (a–e), NO_3 and NH_4 concentrations with elapsed time; (f–j) ρNO_3 uptake rates with elapsed time.

is well simulated for all enclosures (Fig. 8a–e) with some indications of initial lag in the measured decline in NH_4 in the two highest NH_4 addition enclosures, 20 and 30 μmol L^{-1} (Fig. 8d and e). The initiation of NO_3 drawdown is progressively delayed by increasing NH_4 additions (Fig. 8a–e), and is correlated with the decrease in NH_4 to low or near zero concentrations. At 30 μmol L^{-1} NH_4 (Fig. 8e), NO_3 drawdown is not observed even by the final day of the experiment. ρNO_3 (Fig. 8f–j) is progressively delayed with increasing NH_4 concentration. However, the peak ρNO_3 increases with increasing NH_4 concentration up to 20 μmol L^{-1}, a result of the increased time for acceleration of the NO_3 uptake rate. This increase in peak ρNO_3 at later times in the incubation allows all NO_3 to be assimilated by Day 4, the exception is at the 30 μmol L^{-1} where little NO_3 uptake occurs even at that time.

3.5.2. Enclosures from the Sacramento River (“WB09-1′‘) experiment

Enclosure experiments (WB09-1 series) were made with water collected from the Sacramento River, at Garcia Bend, above the Sacramento Regional Waste Water Treatment Plant and at location RM44, below the Plant outfall. Three Garcia Bend experiments were conducted, one with no N amendments, a second with added NH_4 and a third with added NO_3. The RM44 enclosure was not amended. All enclosures were followed for 10 days. Daily samplings were made for nutrients and chlorophyll and for ^{15}N tracer uptake rate measurements at 50% ambient light.

The time series of modeled N concentration and uptake (with $\alpha = 8 \times 10^{-5}\,h^{-2}$) and measured data are show in Fig. 9a–h. The un-amended Garcia Bend enclosure time series of NO_3 and NH_4 drawdown (Fig. 9a) is very similar to the low NH_4, high NO_3 enclosure using Central Bay water (Fig. 7a). With added NH_4 to Garcia Bend water (Fig. 9c) modeled NO_3 and NH_4 drawdown are delayed similar to the pattern in the manipulated Central Bay enclosure with 5 μmol L^{-1} NH_4 added (Fig. 8b), and also very similar to the RM44 enclosure (Fig. 9g) which had elevated initial NH_4 and NO_3. The modeled NO_3 in the NO_3 amended Garcia Bend enclosure (Fig. 9e) was exhausted one day earlier than was observed in the enclosure.

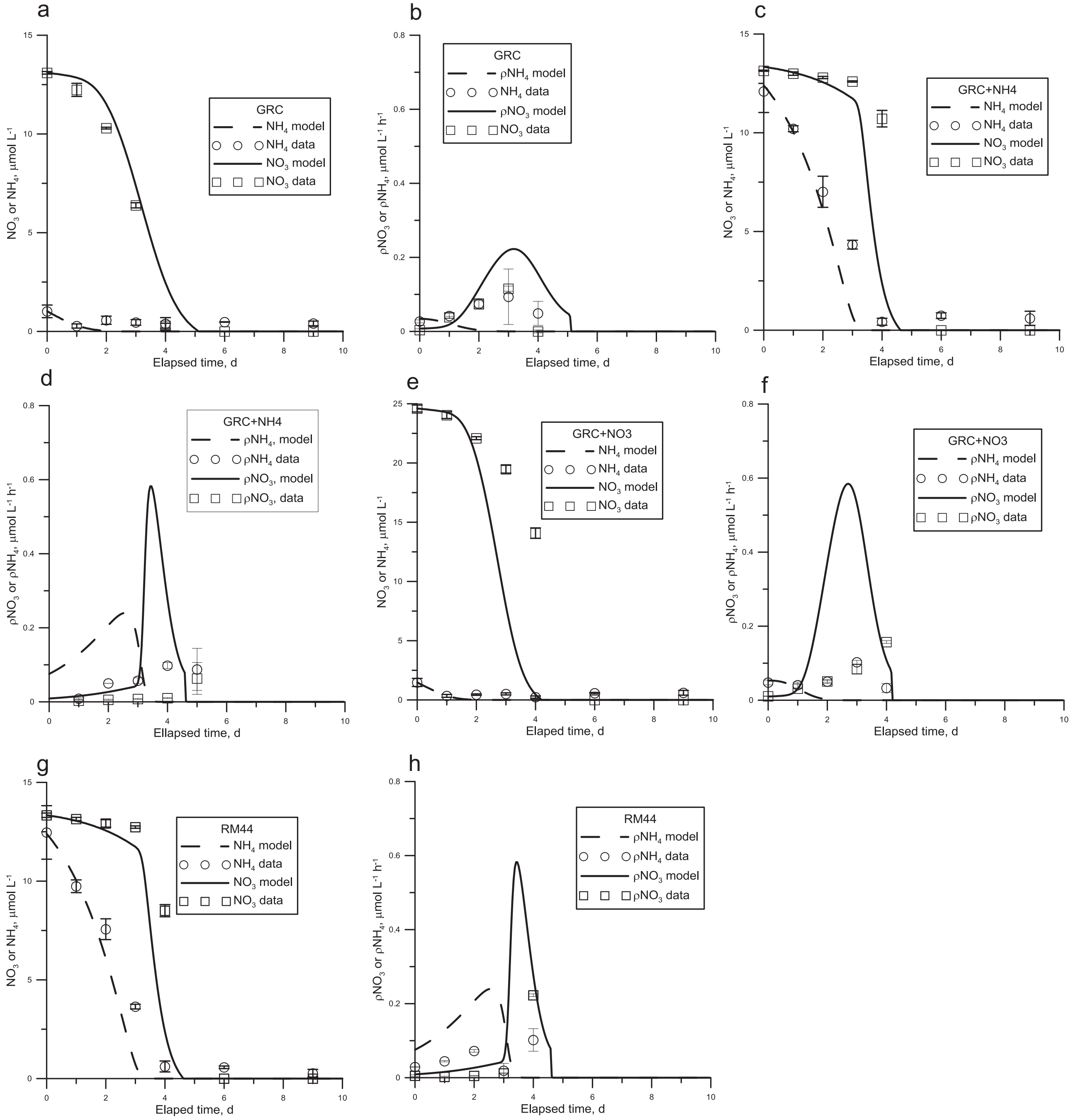

Fig. 9. Time course of modeled (solid line for NO_3, dashed line for NH_4) compared with observed (□ for NO_3, ○ for NH_4) enclosure data (nutrient concentration in a, c, e, g and ρNO_3 or ρNH_4 in b, d, f, h) for four sets of enclosures using water from Sacramento River (WB09-1 experiment). (a and b) water collected from Garcia Bend (GRC); (c and d) water collected from Garcia Bend with added NH_4; (e and f) water collected from Garcia Bend with added NO_3, (g and h) water collected from location RM44.

In the two high NH_4 enclosures, ρNH_4 as modeled overestimated the measured uptake rates (Fig. 9d and h), but the agreement between time series of modeled and observed NH_4 concentrations (Fig. 9c and g) suggests the measured ^{15}N uptake data may be in error. Modeled ρNO_3 was in good agreement with measured rates in the un-amended Garcia Bend and RM44 enclosures (Fig. 9b and h), but were higher than measured uptake in the two amended enclosures (Fig. 9d and f) suggesting a problem with the ^{15}N measurements. In the case of the NO_3 amended Garcia Bend enclosure (Fig. 9e and f) the modeled increase in ρNO_3 due to shift-up (acceleration) by increased NO_3 did not occur in the measured enclosure results. The measured peak in ρNO_3 in the enclosure would have occurred after 4 days, as NO_3 was drawn down in the enclosure (Fig. 9e). However no uptake measurements with $^{15}NO_3$ were made at that time.

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

A set of enclosures with water collected in Central Bay, Suisun Bay, Rio Vista in the Sacramento River and at Ward Island in the lower San Joaquin River (Fig. 1) were sampled daily as in the previous experiments. Concentrations and uptake of NH_4 and NO_3 are plotted against elapsed time in Fig. 10a–h. Modeled drawdown of NH_4 and measured data (Fig. 10a, c, e and g) are in very good

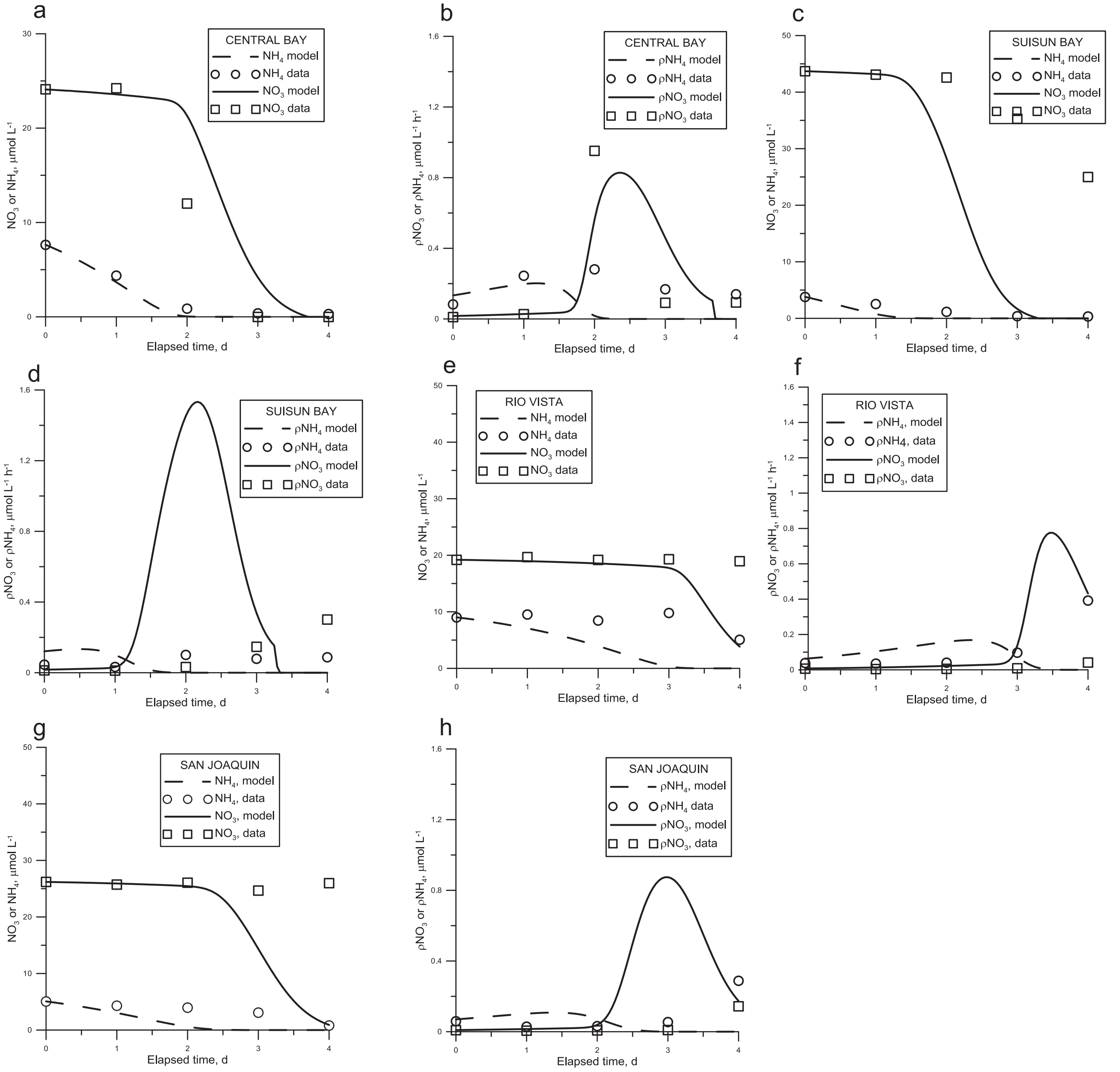

Fig. 10. Time course of modeled (solid line for NO_3, dashed line for NH_4) compared with observed (□ for NO_3, ○ for NH_4) enclosure data (nutrient concentration in a, c, e, g and ρNO_3 or ρNH_4 in b, d, f, h) for enclosures ("Bad Suisun study 3") using water from (a and b) Central Bay; (c and d) Suisun Bay; (e and f) Rio Vista; (g and h) San Joaquin River.

agreement with Central Bay and Suisun Bay (Fig. 10a and c) but not for Rio Vista and San Joaquin (Fig. 10e and g) where no change in NH_4 occurred until Day 4 in the enclosures. The timing of modeled NO_3 decline in the Central Bay enclosure was slower than the measured data, but measured pattern is correct (Fig. 10a). The modeled peak and timing of ρNO_3 in Central Bay (Fig. 10b) are in agreement during the first two days, but measured ρNO_3 in Days 3 and 4 when the NO_3 concentrations were zero was likely an artifact of the added NO_3 substrate as part of the ^{15}N inoculation.

Modeled NH_4 decline and observed data are in agreement in the Suisun Bay enclosure (Fig. 10c). However, measured NO_3 declined more slowly than modeled results. Modeled ρNH_4 is higher than data in the first two days (Fig. 10d). The measured NH_4 uptake rates after Day 2 are higher than modeled, again, likely due to the NH_4 substrate enhancement from ^{15}N additions at low NH_4 concentrations. The modeled peak in ρNO_3 at low NH_4 concentrations (Fig. 10d) was not observed in the data, where NO_3 uptake begins to increase in the last two days, as NO_3 concentrations in the enclosures begins to decrease. Some unknown factor appears to be selectively depressing NO_3 uptake in the Suisun Bay enclosure (Parker et al., 2012a). Trace metal leakage from paint from a large number of anchored naval ships (the U.S. Naval Reserve or "mothball fleet") is one possibility (NOAA Office of Response and Restoration, 2009). Herbicides applied for agricultural weed control and marsh restoration are also sources of toxicity (Blaser et al., 2011; Blaser, 2012).

At Rio Vista, the disparity in NO_3 uptake between model output and measured data (Fig. 10f) is even more severe than in the Suisun Bay enclosure (Fig. 10d). NH_4 concentration drawdown is delayed until the end of the experiment, while modeled NH_4 concentration declines throughout the enclosure period and reaches zero after Day 3 enabling NO_3 decline (Fig. 10e). However, the data show no decline in NO_3 throughout the experiment. Measured ρNO_3

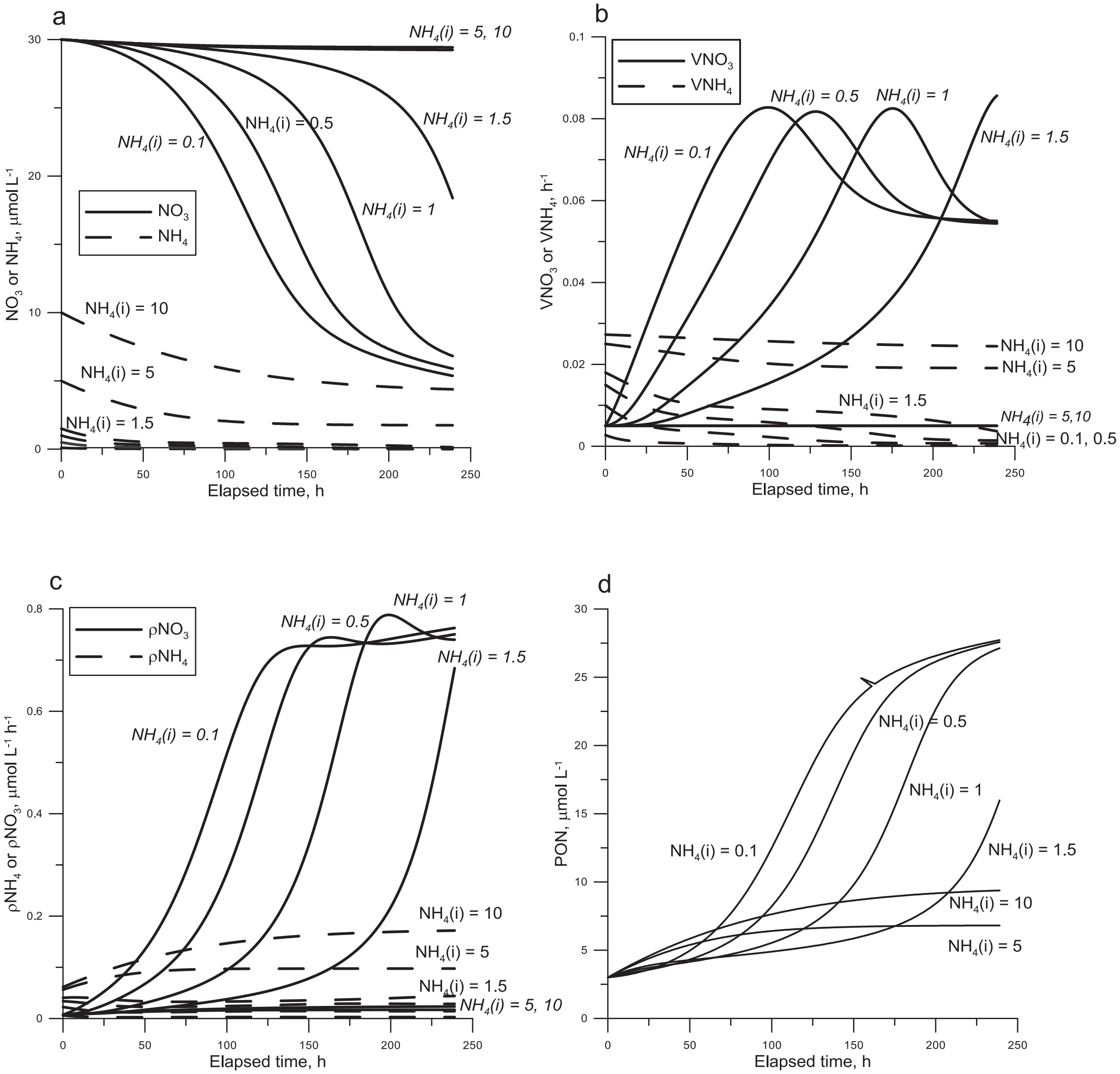

Fig. 11. Model runs with fixed flow (specific flow 0.03 h^{-1}), fully mixed basin, fixed initial NO_3 concentration and variable initial NH_4 concentration. Modeled effect of increasing NH_4 concentrations with elapsed time on (a) concentrations of NO_3 (solid lines) and NH_4 (dashed lines); (b) specific uptake of NO_3 (solid lines) and NH_4 (dashed lines); (c) uptake (ρ) of NO_3 (solid lines) NH_4 (dashed lines); (d) phytoplankton biomass as PON. Italicized initial NH_4 values reflect those used to modeled NO_3 or NO_3 uptake responses.

and ρNH_4 (Fig. 10f) are nearly zero during the first two days and increase slightly toward the end of the time series. The expected peak in NO_3 uptake was not observed as NO_3 uptake rates remained almost zero throughout.

The patterns observed in the San Joaquin River enclosure (Fig. 10 g) most resemble those of the Rio Vista enclosure, with slow NH_4 decline and no NO_3 drawdown (Fig. 10e) low uptake of NH_4 and virtually no NO_3 uptake (Fig. 10 h) all in comparison with the modeled patterns. Comparison of these model simulations with enclosure data provides the basis for moving on to the next level of model with freshwater flow to simulate Suisun Bay.

4. Model runs with freshwater flow

4.1. Model runs with fixed flow, in fully mixed basin mode, with variable NH_4 inflow

The model was run at a fixed specific flow rate of 0.03 h^{-1}, essentially a dilution rate (Flow/Volume) and in this mode represents a hypothetical bay of 1 m^3 volume or any multiple thereof keeping Flow/Volume = 0.03. The model was run with six NH_4 concentrations from 0.1 to 10 µmol L^{-1}; other parameters as in the non-flow model runs. After 240 h, (10 days) the development of a phytoplankton bloom, simulated by turning on irradiance with a fully mixed water column and a uniform vertical light field is shown in Fig. 11a–d. The same basic sequence shown in the enclosure model runs and data occurs with a decline in NO_3 after a decline in NH_4 concentration to low, near zero values (Fig. 11a). NO_3 is drawn down to concentrations of 5–7 µmol L^{-1} within 10 days, except at the highest NH_4 concentrations (5 and 10 µmol L^{-1}) when no drawdown occurs within the 10 day (240 h) period (Fig. 11a), a consequence of the continued elevated NH_4 concentrations at these two highest initial NH_4 inputs.

Specific NO_3 uptake, VNO_3, increases with elapsed time (Fig. 11b); however, the peak in VNO_3 is delayed at higher inflowing concentrations of NH_4 up to 1.5 µmol L^{-1} and then VNO_3 falls to nearly zero at NH_4 concentrations of 5.0 µmol L^{-1} and greater. VNH_4 increases with greater inflowing concentrations of NH_4

according to the Michaelis-Menten kinetics built into the model, but shows no increase with time and remains well below the peak values of VNO$_3$ (Fig. 11b).

ρNO$_3$ (Fig. 11c), follows closely that of VNO$_3$ with peak values delayed and increasing as NH$_4$ concentrations increase and falling to zero at initial NO$_3$ concentrations of 5.0 μmol L^{-1} or greater. ρNH$_4$ uptake (Fig. 11c) increases with time, even as the VNH$_4$ declines, due to the increasing PON biomass. Increases in PON are delayed with increasing inflowing NH$_4$ concentrations (Fig. 10d).

With inflowing NH$_4$ up to 1 μmol L^{-1} a maximum biomass (as PON) of ~30 μmol L^{-1} is achieved after 10 days (240 h) and is based primarily on the assimilation of NO$_3$ (Fig. 11d). At inflowing NH$_4$ of $\geq$5 μmol L^{-1} PON only reaches <10 μmol L^{-1} (Fig. 11d). These plots show clearly the two states of a modeled bay phytoplankton-nitrogen ecosystem, with most inflowing NO$_3$ exported unused when NH$_4$ concentrations are higher, $\geq$5 μmol L^{-1} (Fig. 11a). Fig. 11d shows PON accumulation occurs when NO$_3$ is accessed (Fig. 11c) and NH$_4$ is low (i.e. NH$_4$ < 1 μmol L^{-1}) in contrast to low PON accumulation with NH$_4$ $\geq$5 μmol L^{-1}.). Intermediate conditions are described by the model with NH$_4$ of 1 to 5 μmol L^{-1}. PON produced from NH$_4$ uptake increases with increased NH$_4$ concentrations, but much less than the levels based on NO$_3$ We ascribe this condition to the NH$_4$ paradox (Dugdale et al., 2012). An illustration of how this can be extended to field conditions uses data from Central Bay (next to the Golden Gate). This SFE ecosystem in summer has an NH$_4$ concentration of 5.3 μmol L^{-1} (Wilkerson et al., 2006). The model would predict the phytoplankton biomass as PON to be 7 μmol L$^{-1,}$ according to the NH$_4$ curve for NH$_4$(i) = 5 μmol L^{-1} in Fig. 11d. The average measured PON was 10.2 μmol L^{-1}. This is the low PON accumulation state. As a consequence, even though NO$_3$ concentrations are high in the summer in Central Bay (34.4 μmol L^{-1}; Wilkerson et al., 2006) they are not used and the potential source of N for fueling productivity is exported to the ocean. Other estuaries with high NH$_4$ inputs may exhibit this condition (i.e. unused NO$_3$) predicted by the model.

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

As flow is introduced into the model a boundary can be observed where the phytoplankton-nutrient system state drops into the NH$_4$ based, low biomass, low productivity state (Fig. 12) at specific flows (i.e. flow normalized to the volume of a bay, i.e. = F/V) of 0.01–0.02 h^{-1} depending upon the initial NH$_4$ conditions. The critical flow for a productivity system change is higher at lower NH$_4$ concentrations. Above this critical flow rate, there is insufficient residence time available for the assimilation and reduction of NH$_4$ to levels allowing phytoplankton NO$_3$ uptake and PON accumulation.

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

Model runs using estimates of depth-integrated NO$_3$ and NH$_4$ uptake were made at flows from 100 to 2000 m^3 s^{-1} and inflowing concentrations of NH$_4$ from 1 to 10 μmol L^{-1}. Parameters were the same as in previous model run modes (Sections 4.1 and 4.2) however, NO$_3$ and NH$_4$ uptakes were estimated for the euphotic zone assuming that a single, light-saturated (i.e. 50% of surface irradiance) uptake rate was representative for the euphotic zone. The euphotic zone depth (1.05 m) was calculated from a mean Suisun Secchi depth of 0.3 m (Wilkerson et al., 2006) and the empirical relationship between Secchi depth and light attenuation coefficient as determined for Suisun Bay by Kimmerer et al. (2012). The euphotic zone N uptake was scaled to the ratio of the euphotic zone depth to the mean depth of Suisun Bay (5.61 m) and provided in these runs as depth-integrated N uptake values. Model runs were made for 30 days. Final values of PON are contoured in Fig. 13 on a NH$_4$-flow plane. These contours show the two state ecosystem with a sharp transition from high, NO$_3$ based productivity (i.e.

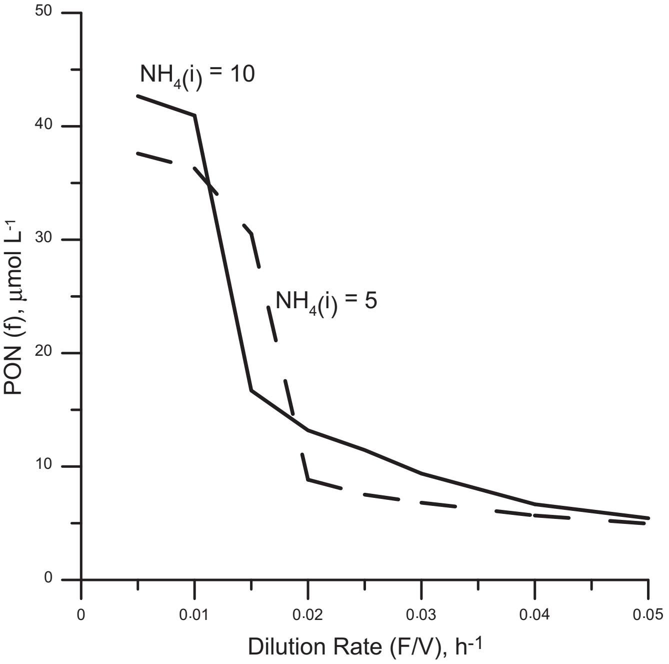

Fig. 12. Model runs with varying flow, in fully mixed basin mode with fixed NH$_4$ inflow concentrations. Effect of variable specific flow rate (F/V, h^{-1}) and initial NH$_4$ of 5 or 10 μmol L^{-1} on the final PON concentration resulting after 240 h.

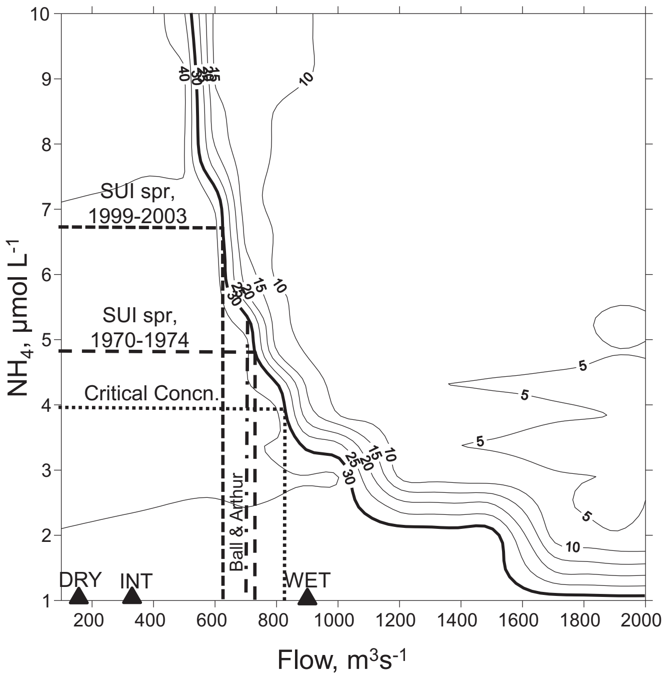

Fig. 13. Model runs with varying flow a fully mixed water column, with depth-integration allowing for light limitation. Effect of flow and initial NH$_4$ concentrations on final PON concentrations (in μmol L^{-1} as contours with 30 μg L^{-1} in bold). Arrows show flows in dry, intermediate and wet water years from Peterson et al. (1985). Horizontal dashed lines plotted are mean NH$_4$ concentrations (for spring 1970–1974 and 1999–2003) or criterion extended to the 30 μg L^{-1} contour and projected to the flow axis (x-axis). The Ball and Arthur (1979) vertical line is set at the maximum flow at which chlorophyll blooms were observed.

high PON concentrations) to low, NH_4 based productivity (i.e. low phytoplankton biomass) delineated by the 30 μmol L^{-1} PON contour. At high NH_4 concentrations (5–10 μmol L^{-1}) the contour lines are nearly vertical and small changes in flow result in a transition from one productivity state to the other. High NH_4 concentrations restrict the maximum flow to ~600 $m^3 s^{-1}$ for high productivity. Changes in NH_4 concentration have far less effect than flow in this region. Below NH_4 of 5 μmol L^{-1}, the critical flow increases with decreasing NH_4 concentration to about 2 μmol L^{-1} where the contours are horizontal and small changes in NH_4 concentration can result in a state transition; flow is less important than NH_4 in this region. In summary, low NH_4 concentrations allow higher flows for the high productivity (biomass) condition (up to 1500 $m^3 s^{-1}$) and are more important than flow in this region for determining productivity condition.

5. Discussion

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

The model when run in the no-flow mode provides a diagnostic tool for interpretation of enclosure experimental data, offering mechanisms for phytoplankton and N interactions and suggesting next steps in understanding anomalous phytoplankton environmental conditions in the field. In some situations, modeled responses of NH_4 and NO_3 uptake and N drawdown agreed well with field data from a variety of enclosure experiments using water sampled from estuarine locations other than the location originally used to calibrate the model (i.e. Central Bay). In others, comparison of modeled results with data revealed conditions where patterns of phytoplankton uptake of NH_4 or NO_3 and biomass accumulation did not agree with the model. For example, the enclosures filled with water from Rio Vista (Fig. 10e) showed relatively slow NH_4 drawdown compared to modeled expectations, accompanied by delayed NO_3 drawdown, suggesting a growth-limited condition. These anomalous conditions that do not fit our modeled view of NH_4 and NO_3 interaction, are likely due to other parameters in the water, such as dominance by species other than diatoms and factors that directly affect N uptake and growth, e.g. herbicides (Blaser, 2012). Similar observations were made by Parker et al. (2012a,b) in experimental enclosures filled with water from a station in western Suisun Bay. The Suisun Bay enclosure (Fig. 10c) showed typical NH_4 drawdown but slow NO_3 drawdown compared to model results, suggesting a problem specific to NO_3 uptake, possibly unknown toxins affecting NO_3 transporters or the enzyme nitrate reductase. The usefulness of the model in these two cases is to provide suggestions for appropriate experiments, such as Toxicity Identification Evaluations (TIE's) (e.g. US EPA, 1988) to isolate the specific problem causing the observed effects.

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

Phytoplankton blooms in Suisun Bay prior to 1987 were accompanied by complete drawdown of initial NH_4 and NO_3. Using data collected from 1969 to 1977 Ball and Arthur (1979) observed DIN to decline in the summer in Suisun Bay, to limiting concentrations, <0.02 mg N L^{-1} (1.4 μmol L^{-1}) with peak summer concentrations of chlorophyll of 40–100 μg L^{-1}. Similarly, this was observed in Honker Bay (in Suisun Bay, Fig. 1) in 1970 by Di-Toro et al. (1977, their Fig. 13) who reported NH_4 concentrations to decline from 0.07 mg L^{-1} (5.0 μmol L^{-1}) in May to undetectable in July and NO_3 from 0.4 mg L^{-1} (28.6 μmol L^{-1}) to undetectable in July, when chlorophyll concentrations reached 50 μg L^{-1}. These pre-1987 blooms were supported by both NH_4 and NO_3 and were in the high biomass, NO_3 utilization state analogous to the high biomass state predicted by the SFE biogeochemical flow model, i.e. in the area of Fig. 13, to the left of the 30 μg L^{-1} PON contour.

The mean spring NH_4 concentration for the years 1970–1974 (SUI spr. 1970–1974 in Fig. 13) in Suisun Bay (Station D6) of 4.95 ± 1.49 μmol L^{-1} (Ball, 1977) is plotted on the y-axis of Fig. 13. A horizontal line dawn from this NH_4 concentration intersects the 30 μg L^{-1} PON contour at a flow rate of ~700 $m^3 s^{-1}$ (vertical line drawn to the x-axis), setting the maximum flow rate that would allow a high biomass bloom to occur. Ball and Arthur (1979) considered the Suisun Bay phytoplankton standing crop before 1976 to be related directly to water transparency and indirectly to Delta outflow (i.e. river flow) and concluded that only when the outflow varied between 110 and 700 $m^3 s^{-1}$ did chlorophyll concentrations of >20 μg L^{-1} occur in the entrapment zone adjacent to the shallows of Suisun/Honker Bay, the same maximum flow predicted by the model for the mean NH_4 concentration.

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

More recently (1999–2003) the mean spring NH_4 concentration in Suisun Bay was 6.8 μmol L^{-1} (Wilkerson et al., 2006) which intersects the 30 μmol L^{-1} PON contour near 600 $m^3 s^{-1}$ (Fig. 13), setting an upper flow limit for high biomass accumulation slightly lower than the prediction from the pre-1987 data (~700 $m^3 s^{-1}$). Another prediction of the maximum flow rate for bloom formation is obtained by plotting the 4 μmol L^{-1} NH_4 concentration criterion below which NO_3 uptake occurs and bloom formation begins (Dugdale et al., 2012) on the *y*-axis of Fig. 13, yielding a maximum flow rate of just over 800 $m^3 s^{-1}$.

Over the range of NH_4 concentrations from 4.0 to 6.8 μmol L^{-1}, predicted maximum river flow rates range narrowly from 600 to 800 $m^3 s^{-1}$ in good agreement with the maximum river flow, 700 $m^3 s^{-1}$ suggested by Ball and Arthur (1979). Two large blooms were observed in Suisun Bay from mid-April to the end of May 2010. The mean Delta Outflow during that period was 644.5 ± 113.9 $m^3 s^{-1}$ just below the maximum flow (700 $m^3 s^{-1}$) described by Ball and Arthur (1979), and also below the modeled estimate of maximum flow (800 $m^3 s^{-1}$) for the 4 μmol L^{-1} NH_4 concentration criterion. The mean Delta Outflow 2010 flow during the bloom period was also below the washout flow criterion of 1100 $m^3 s^{-1}$ calculated by Dugdale et al. (2012), above which phytoplankton populations are washed out and cannot bloom. This washout criterion is based on the mean spring NH_4 uptake rate of the phytoplankton in Suisun Bay (Dugdale et al., 2012) and above that flow rate, the growth rate of the phytoplankton is less than the loss rate due to flow and the population is washed out and shows zero growth or net loss.

In addition to NH_4 and flow impacts on phytoplankton blooms, grazing by invasive clams (*Potamocorbula amurensis*) could contribute to declining chlorophyll concentrations and lack of spring blooms although clams are in low concentration and size in spring (Greene et al., 2011). However, as discussed in Dugdale et al. (2012) clam abundance in Suisun Bay was unchanged in spring 2010, when there was a phytoplankton bloom, and were monitored at similar densities to previous years (in spring) when blooms were absent.

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

The mean river freshwater flows in spring for wet, intermediate and dry years (Peterson et al., 1985) are shown as arrow heads drawn on the *x*-axis. The model in its present form suggests that dry and intermediate years should allow phytoplankton blooms (i.e. PON > 30 μmol L^{-1}, equivalent to chl > 30 μg L^{-1}; Dugdale et al., 2012) at NH_4 concentrations up to 10 μmol L^{-1}. However, in wet years, NH_4 concentrations would have to be $\leq$ 4 μmol L^{-1} for blooms to occur.

5.5. Model predictions of spring bloom occurrences in Suisun Bay

The similarity in freshwater flow relationship to phytoplankton blooms in Suisun Bay in the 1970s and recently in 2010, leads to the suggestion that the mechanism behind the earlier blooms was essentially the same as presently observed in Suisun Bay when NH_4 concentrations are low (Wilkerson et al., 2006; Dugdale et al., 2007, 2012). This mechanism requires that phytoplankton be able to access the available NO_3 for growth which does not happen when NH_4 concentrations are high. The with-flow model results are consistent with this view. The model results are also consistent with the conclusion of Jassby (2008) that biomass accumulation is inversely related to freshwater flow, a consequence of reduced residence time with increased flow.

However, the model predicts high biomass with any concentration of NH_4 up to 10 μmol L^{-1} and flows of less than 500 m^3 s^{-1} (intersection of 10 μmol L^{-1} NH_4 with the 30 μg L^{-1} PON). Typically low flows would be expected in the summer. However, high levels of biomass do not occur in summer and have only been observed rarely in spring (i.e. Wilkerson et al., 2006; Dugdale et al., 2012). In the model any factor that reduces the rate at which NH_4 concentrations decline or that add to the NH_4 concentration will extend the period without NO_3 uptake and prevent biomass accumulation. High rates of benthic regeneration of NH_4, unaccounted-for sources of NH_4 (e.g. waste water treatment plants) and high grazing rates by either benthos or zooplankton would have such an effect. None of these possibilities are considered in the present model. Clam biomass and grazing is highly seasonal and may be the most likely source of regenerated nitrogen as NH_4 in summer and fall.

The model could be expanded in several ways. Both clam and zooplankton grazing could be added to the model in the near future. Exchange of NH_4 with the sediment has been measured in Suisun Bay (J. Cornwell, personal communication) at rates that suggest it will be necessary to include this source/sink in the model. Pelagic nitrification (NH_4 oxidation to NO_3) by bacteria and archaea has been estimated to be greater than phytoplankton NH_4 uptake in the Sacramento River (Parker et al., 2012a,b) and consumes oxidation in the process of producing NO_3. A nitrification pathway needs to be included in a future model. Then rates of nitrification measured with ^{15}N (Parker, personal communication) should be compared to the model estimates. These enhancements to the model would provide a more complete description of the pattern of NH_4 fluxes and concentrations with time. Other phytoplankton functional groups such as cyanobacteria could also be added. Ongoing studies of the effect of NH_4 concentration and N:P ratio will provide data for validation of the enhanced model. Toxicity of NH_4 to diatoms has not been included in the current model. However, NH_4 inhibition of NH_4 uptake by phytoplankton has been shown to occur in the Sacramento River when NH_4 concentrations are >20 μmol L^{-1}. Such high concentrations of NH_4 have not been observed in the source waters to Suisun Bay. To make the model functional for the Sacramento River such an inhibition term could be added.

5.6. Future uses for the model

The model results suggest that reduction in inflowing NH_4 concentrations to Suisun Bay would reduce or eliminate the NH_4 sensitivity of phytoplankton biogeochemical processes in the Bay. With these NH_4 reductions, spring phytoplankton bloom occurrence would be dependent upon freshwater flow conditions, strongly improving the likelihood of blooms and food supply to pelagic organism decline species. On the other hand, proposed increases in freshwater flow, to provide more suitable habitat for the delta smelt, would be predicted to have no significant effect on phytoplankton productivity if NH_4 concentrations were low, but could quite drastically reduce the biomass of phytoplankton at the present mean NH_4 concentrations (e.g. 6.8 μmol L^{-1} in Suisun Bay) (Fig. 13).

The present model is one dimensional and nitrogen-based, and at this point should be regarded as a step in the development of a full three dimensional model of the SFE/Delta system. This tool will help elucidate the pre-1987 ecosystem processes and evaluate the impact of management and regulatory strategies. A unique aspect of the present model is the inclusion of terms for the time varying rate of maximum NO_3 uptake as a function of NO_3 concentration (acceleration) and for inhibition of NO_3 uptake by NH_4. The model of Di-Torro et al. (1977) included a mechanism for considering preferential use of NH_4 and NO_3 uptake by estuarine phytoplankton, ensuring that NH_4 is used before NO_3. However, the likely role of NH_4 in creating a stable two-state productivity (biomass) ecosystem and modulating the flow-bloom pattern in Suisun Bay has not been considered before. The modeled phytoplankton biomass in the two states of Suisun Bay may be analogous to previously existing ecosystem states of the SFE described by Glibert et al. (2011). The modeled high biomass, NO_3 based, high productivity state would be analogous to the pre-1982, diatom era with large copepods (*Eurytemora*) and delta smelt (Glibert et al., 2011). The modeled low biomass, low productivity state based on NH_4 would be analogous to the post 1982 cryptophyte/flagellate era with small copepods (*Pseudodiaptomus*) with bass and shad. Glibert et al. (2011) attribute the change in food web components to the shift in the dominant form of DIN, NH_4 becoming more dominant post 1982.

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

Acknowledgments

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Long-Term Changes in Nutrient Loading and Stoichiometry and Their Relationships with Changes in the Food Web and Dominant Pelagic Fish Species in the San Francisco Estuary, California

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Nutrient enrichment is an important stressor in coastal ecosystems. This analysis tests the hypothesis that changes in nutrient loads, imbalances in nitrogen:phosphorus, and changes in nitrogen form, especially shifts to increasing loads of chemically reduced, rather than oxidized nitrogen, can have major impacts on food webs, from primary producers through secondary producers to fish. The application of cumulative sums of variability, the running total of deviations from normalized values over time, is a sensitive method for comparing rates of change between and among all parameters, including organisms of all trophic levels. This approach was applied to the San Francisco Estuary, California, demonstrating that abrupt changes in nutrient loads and nutrient form over the past several decades were correlated with food web changes, including pelagic fish collapse. Remediation of pelagic fish populations should be centered on reduction of nitrogen loads and reestablishment of balanced nutrient ratios delivered from point source discharges.

Keywords ammonium, CUSUM charts, delta smelt, eutrophication, nutrient ratios, nutrient stoichiometry, pelagic organism decline, plankton trophodynamics

INTRODUCTION

The San Francisco Estuary, California, which encompasses the Sacramento-San Joaquin Bay Delta, is one of the largest estuarine systems on the Pacific Coast as well as one of the largest managed and engineered water systems in the United States. It is the largest source of municipal and agricultural fresh water in California and is home to economically important fisheries. Major modifications to this system have occurred over the past century, including drainage of marshes to support agriculture, installation of dikes to prevent farmland flooding, expansion and deepening of shipping lanes, and significant diversion of water to various users throughout the state (Atwater et al., 1979). The Bay Delta system, an inverse delta, receives the majority of flows from the Sacramento and San Joaquin Rivers, of which the Sacramento is the largest (Atwater et al., 1979; Nichols et al., 1986). The Bay Delta ecosystem has also been significantly modified by invasive species, including clams, bay grasses, various species of copepods, and fish over the past several decades (Cohen and Carlton, 1998; Kimmerer, 2002).

The Bay Delta is the subject of considerable national public awareness due to the sociopolitical and socioeconomic tension surrounding the plight of the endemic delta smelt (*Hypomesus transpacificus*), a small (length ca. 6 cm) fish whose decline has been taken as a sign of adverse environmental conditions in the region. The delta smelt was put on the Threatened Species list in 1993 (Wanger, 2007a, 2007b) and has since undergone further significant population decline along with longfin smelt (*Spirinchus thaleichthys*), threadfin shad (*Dorosoma petenense*) and young-of-the-year striped bass (*Morone saxatilis*; Manly

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and Chotkowski, 2006). Accelerated losses during the last decade have been termed the "Pelagic Organism Decline" (POD) period (Sommer et al., 2007). In recent years, the Federal court, under the Endangered Species Act, has ordered modification of water diversion projects to protect the smelt (Wanger, 2007a, 2007b). Presently, a National Academy of Sciences panel has been convened in order to prepare a report for the U.S. Congress on sustainability and the planned water management options for the Bay Delta (NRC, 2010).

To date, no single ultimate cause of the POD has been identified, and the interpretation of data has favored a conclusion that multiple stressors combined to cause a population collapse (Sommer et al., 2007; MacNally et al., 2010; Thompson et al., 2010). Among the major factors that are thought to stress the delta smelt and other pelagic organisms are modification of the natural hydrology of the system, including export pumping for domestic and agricultural water use, habitat changes that affect recruitment (reproduction), invasion of exotic species including toxic algae, toxin loading, climate change, and food web modification through changes in species and predation (Linville et al., 2002; Lehman et al., 2005; Bennett, 2005; Sommer et al., 2007; Davis et al., 2008; Jassby, 2008). Because each of these physical, chemical and biological factors potentially influences and modifies other factors, the system as a whole is highly complex and prior efforts that used standard multifactor correlative analyses of 30 years of ecosystem data have not been successful at identifying causality with any degree of certainty (Bennett and Moyle, 1996; Sommer et al., 2007; MacNally et al., 2010; Thompson et al., 2010).

Of considerable interest has been the effect of export pumps on pelagic fish. The extent of withdrawals of water for human and agricultural consumption is on the order of 20–25% of the inflowing water (Jassby, 2008), and there is no question that these operations have had large effects on the ecosystem. Flow is rigorously managed through engineering of the isohaline where salinity is equal to 2; this isohaline is measured as the distance from the Golden Gate Bridge and is locally referred to as X2 (Jassby et al., 1995; Kimmerer, 2004). Given the current state of decline of the pelagic fish, restrictions on water pumping have been imposed in recent years, resulting in public, economic, and political tensions (NRC, 2010). It has been thought that regulation of flow will lead to improved conditions for endangered fish.

It is also well recognized that the flows of energy and materials through the food web of the San Francisco Estuary are complex and not well understood. The frequent changes, invasions, and effects of engineering and other management actions also make these relationships complicated to interpret. Some investigators have suggested that the food web of the Bay Delta is sensitive to alterations in nutrients. However, no effort to date has focused on regulation of nutrients as a means to improve the declining fish. Yet, it has been reported, based on experimental data, that high ammonium (NH_4^+) levels inhibit diatom growth, thus, potentially restricting the availability of a preferred food source in the food chain that supports fish (Wilkerson et al., 2006; Dugdale et al., 2007). Moreover, changes in nitrogen:phosphorus (N:P) ratios of nutrients in the water have been correlated with overall declines in water column chlorophyll a (chl *a*) of the Bay Delta in the mid-1990s (Van Nieuwenhuyse, 2007).

The possibility of "bottom up" control of fish populations in this system has been largely dismissed for several reasons: most nutrients are at levels that saturate (maximize) phytoplankton growth; phytoplankton growth is considered to be regulated primarily by light limitation (Cole and Cloern, 1984); NH_4^+ is generally a preferred form of nitrogen for phytoplankton uptake; the pH of the receiving waters prevents formation of the toxic compound, ammonia gas (NH_3); and the NH_4^+ levels are typically below the criteria considered by the U.S. Environmental Protection Agency (EPA) for fish habitat (McCarthy et al., 1977; Millero, 2006; Jassby, 2008; U.S. EPA, 2010). In addition, some analyses of nutrient effects have considered only total N or P and chl *a*, rather than nutrient form and phytoplankton composition (e.g., Jassby, 2008). As a consequence, relationships between nutrients, production or food web effects have been ambiguous, leading to indecisive conclusions, as noted by Jassby (2008), "The physiological effect of ammonium . . . may well play a role in the dynamics of specific phytoplankton events. . . . But it is one factor among many, and its ecological effect relative to other sources of variability underlying long-term phytoplankton patterns is not yet clear."

In contrast to conditions in the 1960s and early 1970s in this system, when hypoxia was more frequently noted (Nichols et al., 1986), there are presently no widespread classic symptoms of eutrophication (e.g., Cole and Cloern, 1984; Kimmerer, 2004), although localized hypoxia has been reported and increased frequency of cyanobacterial blooms in the past decade has been noted (Lehman et al., 2005; 2008). Improvements in sewage treatment in the 1980s, in response to the U.S. Clean Water Act, as well as other nutrient removal efforts, are generally credited with minimizing symptoms of eutrophication. Ironically, as will be shown below, these changes in sewage treatment and other nutrient removal efforts may have had unintended consequences on the food web, that, while reducing the classic symptoms of eutrophication, may have resulted in significant biotic responses that propagated through the food web.

Shifts in algal composition and food availability have been suggested as an important factor in fish decline, especially in the past decade, not only because of the increasing frequency and range of blooms of the cyanobacterium, *Microcystis aeruginosa* (Lehman et al., 2005, 2008), but because of declines in diatoms and increases in flagellates (Lehman, 1996; Müller-Solger et al., 2002, Brown, 2010). Yet, how and why these phytoplankton groups have changed has not been understood. As noted by Kimmerer (2004), "we do not really understand the controlling factors of some of the important fishes and invertebrates of the estuary. We have almost no information on the dynamics of energy flow in higher trophic levels, or how these levels are limited by productivity at the base of the food web." The current analysis attempts to begin to understand these relationships from a broad, long-term perspective. Key pathways of nutrient effects were discerned from the analysis herein. Nevertheless, Kimmerer's (2004) analysis continues to stand correct in that much remains to be understood with regard to understanding the dynamics and mechanisms of nutrient flow and its effect on trophodynamics.

The quality (form) of N has long been recognized to influence the relationship between primary producers and fish. Within the field of oceanography, NO_3^--based food webs are thought to lead to fish (export) production while those based on NH_4^+ more generally support retentive or microbial food webs in nutrient-depleted marine systems, based on the classic concept of "new" and "regenerated" production (Dugdale and Goering, 1967; Eppley and Peterson, 1979; Glibert, 1988). However, the extent to which this dichotomous control of food webs applies in nutrient-enriched coastal systems is unclear. These systems receive significant inputs of "new" N in reduced form and therefore the question remains as to whether total nutrient load or form controls food webs when loadings are high (e.g., Nixon and Buckley, 2002). The fundamental ecological question is: How does the nutrient signal propagate through the food web? It has previously been suggested that variance in state variables changes with regime shifts or disturbance (e.g., Carpenter et al., 2007), but examples of trophic changes due to nutrient changes in highly impacted coastal systems are rare.

This analysis focuses on some of those pelagic species whose populations have changed significantly in the San Francisco Estuary over the past decade or more: delta smelt, longfin smelt, striped bass, largemouth bass (*Micropterus salmoides*), inland silversides (*Menidia beryllina*), threadfin shad (*Dorosoma petenense*), and sunfish (*Lepomis* spp.). The delta smelt has undergone significant population declines in the past few years, along with longfin smelt, threadfin shad, and striped bass, while largemouth bass, inland silversides, and sunfish, among other species have recently increased in abundance (Kimmerer et al., 2000; Bennett, 2005; Rosenfield and Baxter, 2007). The latter trends have led to suggestions that increased predation is another factor contributing to declines in smelt and other POD species.

The goal of this analysis is to identify key relationships between nutrient concentrations, forms, ratios, and sources and the major components of the food web, from phytoplankton to zooplankton, clams, and fish, based on the 30-year term time series from the San Francisco Estuary. In particular, the hypotheses that increased NH_4^+ loading relative to NO_3^-, as well as changes in nitrogen (N) and phosphorus (P) stoichiometry, are related to the changes in dominant fish over time because of their effects on the dominant primary producers. As the dominant functional groups of primary producers in the system changed, so, too, did the food web leading to fish. Accordingly, this analysis also explores the relationships between nutrient availability and form on the invasive clam, *Corbula amurensis,* as well as its relationship to the food web.

This analysis applies the cumulative sums of variability (CUSUM) approach (Page, 1954) to identify trends in nutrients, plankton communities, and fish over time. Comparisons of CUSUM charts of time series data can detect changes not readily apparent in mean values (e.g., Manly and Mackenzie, 2003; Mesnil and Petitgas, 2009), and they are sensitive to the timing and directional change in trends. This approach, displaying a running total of deviations from normalized values, was used to compare changes between and among all parameters, i.e., from nutrients to the trophic links to fish. The CUSUM approach, commonly used in some other disciplines, has not been previously applied in an end-to-end (*sensu* Steele et al., 2007) ecological assessment. It provides a powerful tool to test whether a particular variable drives ecosystem change. It is an alternative to complex, multi-parameter, nonlinear models of food web interactions that are often limited by available data or knowledge of key interactions.

These nutrient and trophodynamic relationships developed here are also contrasted with those of system water flow. In total, nutrient availability and stoichiochiometry were found to be more strongly correlated with long-term changes in dominants in each tropic level than was water flow over a multi decadal period. Lastly, given the scientific, management and legal issues related to water management in the Bay Delta, specific management recommendations are suggested for nutrient control that have high probability for success in restoring endangered pelagic fish.

MATERIALS AND METHODS

Site Description

The estuary consists of South San Francisco Bay, Central Bay, San Pablo Bay, Suisun Bay and the Sacramento-San Joaquin Bay Delta, a complex of rivers, channels, wetlands, and floodplains (Figure 1; Atwater et al., 1979; Nichols et al., 1986; Müller-Solger et al., 2002). With exception of the deeper Central Bay, the mean depths of the various sub-embayments in the estuary range from 3.3 to 5.7 m (Kimmerer, 2004). In the context of estuarine typology (e.g., Madden et al., 2010), Suisun Bay is river-dominated, while the South Bay is lagoonal (Kimmerer, 2004). The focus of this analysis is on Suisun Bay, and its main river source, the Sacramento River. Nutrient data are provided from the lower San Joaquin River for comparison.

The upper reaches of the Sacramento River drain 61,721 km^2, while the upper San Joaquin River drains 19,030 km^2 (Sobota et al., 2009). On a long-term basis, the Sacramento River contributes $>80\%$ of river inflow to the Bay Delta, while the San Joaquin delivers $\sim 12\%$, the remainder coming from minor sources flowing into the Delta from the east (IEP, 2006; Jassby, 2008). River flow has varied by about ten-fold over the past several decades due to effects of El Niño, prolonged droughts, and ENSO wet years (Jassby, 2008).

Overall Approach

A retrospective analysis was conducted of 26 to 30 years (depending on variable), spanning 1975 (or 1979) to 2005, of

Figure 1 Map of the Sacramento-San Joaquin Estuary, with sites of the major wastewater discharge site in the upper Sacramento River, and the sites of data analyzed herein indicated.

monitoring data from the San Francisco Estuary and Bay Delta. Data were obtained from publically available portals that provide long-term monitoring programs of numerous agencies, or, for some recent years, by direct request from state or federal agencies.

Although the sources and brief methodological descriptions are given here of the source data, the reader is referred to the actual sources for more thorough metadata descriptions. The analysis here highlights those species which are either dominants, or which have received considerable attention because they represent invasive species that have had effects on the food web. Note that there are no long-term data available on bacteria, ciliates or most other microzooplankton. Kimmerer (2004) provides a more thorough review of the complexities of the food web for San Francisco Estuary.

Data Sources

Flow data were obtained from the California Department of Water Resources Dayflow record, http://www.water.ca.gov/dayflow/. Dayflow is a computational program that accounts for natural, tidally averaged flows, as well as inflows, exports, and transfers of managed, tidally averaged flow into, within, and out of the Sacramento-San Joaquin Delta (IEP, 2006). The Sacramento outflow data were used here.

All nutrient, chlorophyll *a*(chl *a*) and phytoplankton data were obtained from the Interagency Ecology Program Bay Delta and Tributary project data portal, http://www.bdat.ca.gov/. Nutrient samples were collected from the subsurface on a bimonthly to monthly basis, filtered through Whatman GF/F filters, and frozen until analysis by autoanalyzer techniques. Concentrations of chl *a* were also determined on subsurface samples on a bimonthly to monthly basis. Samples for phytoplankton composition were collected by submersible pump, preserved in Lugol's solution, and subsequently enumerated microscopically to species level. Nutrient data, as NH_4^+ concentration, ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP), and the ratio of oxidized to reduced inorganic forms of N ($NO_3^- + NO_2^-:NH_4^+$) were examined herein. Values for $NO_3^- + NO_2^-$ are referred to as NO_3^-. Phytoplankton data, while available as individual species counts, were grouped into dominant functional groups: diatoms, green algae, cryptophytes, other flagellates, and cyanobacteria. For each function group, values were calculated as average species cell number mL^{-1}. The cyanobacterium *Microcystis aeruginosa* has increased in this system since ~1999 (Lehman et al., 2005), but these data are not included in this analysis because they are not in the long-term data base. Picocyanobacteria are also not included herein because they are not routinely enumerated. Where frequency of data was greater than monthly for nutrients or phytoplankton, monthly averages were calculated.

Zooplankton data were retrieved from the monthly zooplankton surveys conducted by the California Department of Fish and Game (http://www.dfg.ca.gov/delta/). These samples were collected from spring to fall using a Clarke-Bumpus net (154 μm mesh) for meso-zooplankton and, for the micro-zooplankton, a pumped sample was passed through a 43 μm mesh net. All samples were preserved with 5% formalin and subsequently enumerated microscopically. This analysis focuses on 3 dominant copepods species, *Eurytemora affinis*, *Pseudodiaptomis forbesi*, and *Limnoithona tetraspina*. The analysis does not include ciliates, other microzooplankton or mysids, nor does it include bacteria.

Data on the abundance of the exotic clam *Corbula amurensis* were also obtained from the Interagency Ecological program database (http://bdat.ca.gov/). Those samples were collected using a hydraulic winch and Ponar dredge, which samples a bottom area of ~ 0.05 $m^2$and which penetrates to variable depths depending on local conditions. Repeated samples are collected and slurried before enumeration according to Standard Methods for the Examination of Water and Wastewater (1998). In the laboratory, identifications were made using a stereoscopic dissecting microscope (70–120×) or a compound light microscope if needed.

Fish data were obtained from the California Department of Fish and Game (http://www.dfg.ca.gov/delta/). The summer townet surveys (delta smelt only) were conducted by undertaking up to 3, 10-min, stepped, oblique tows using gear with 1.5 m mouth opening attached to a hoop frame and mounted on skis. Surveys were conducted from late June to early August. Fall midwater trawl (FMWT) data were obtained from samples that were collected from 10- min diagonal tows using variable meshes starting with 20 cm at the mouth of the net and tapering to 1.25 cm. One survey was conducted each month from September-December from San Pablo Bay into Sacramento-San

Joaquin Delta. Volume-weighted catch-per-unit-effort data for each survey were summed to produce estimates of annual indices of abundance.

Effluent discharges to the upper Sacramento River were compiled by the State Water Contractors (http://www.swc.org/). Although the Sacramento wastewater treatment plant came on line in 1982, NH_4^+ discharge data are only available beginning in 1992. Annual averages of N and P discharge prior to 1992 have previously been published, (Van Nieuwenhuyse, 2007).

This analysis emphasizes results from the upper Sacramento River station C3, and Suisun Bay stations D8 and D7, although additional NH_4^+ data from the delta region (station D28) are presented for comparison (Figure 1). The intervening region between the upper Sacramento River and Suisun Bay encompasses much of the natural habitat for the delta smelt and the other pelagic fish discussed above.

Statistical Analysis

CUSUM trends were calculated for the 3-decade data record for flow, nutrient concentrations, nutrient ratios, effluent loadings, phytoplankton abundance as chl *a* and as dominant functional groups, and abundance of the major zooplankton, as well as clams and pelagic fish species. There are numerous approaches for CUSUM calculations; the approach herein applies the *z*-score CUSUM method (Page, 1954). All data for which CUSUM scores were calculated were first transformed to *z*-scores. This involves calculation of a "population" mean and standard deviation, where population refers to all data of that parameter in the time series. Each data point (either monthly or annual, depending on the parameter) was normalized by first subtracting the population mean and then dividing the result by the population standard deviation. The second step in the CUSUM approach is to sum all of the *z*-scores over time to obtain a long-term trend. The effect of such manipulation is to filter the short term or seasonal variance, thereby revealing the long-term patterns in the data.

Although not equivalent, the trends in CUSUM over time for time series data are similar to long-term running averages (Glibert et al., in review). It is the change in CUSUM over time, or the comparison of CUSUM changes in one parameter relative to another, that is of interest. Absolute CUSUM values are not important to the understanding of relationships. Absolute CUSUM values will change depending on the length of the time series, as inclusion of additional data will change the "population" mean and standard deviation. CUSUM curves are particularly useful in identifying change points, or periods when the long-term mean changes from being, for example, above the long-term mean to below the mean. These points in time are identified from inflection points on the curves. Downward trends in CUSUM charts indicate values below the long-term mean and upward trends indicate values above the long-term mean.

If CUSUM charts of two different variables exhibit similar ascendency, descendency, and inflection points, the changes in these variables are correlated. In relating CUSUM charts of one variable to another, it is recognized that such correlations do not equate to correlations of the raw data. The former is a comparison of how the long-term trends in the variables compare, whereas the latter is a comparison of how the concentration of individual parameters compare at any one point in time. Relationships between CUSUM trends for different nutrients or between different components of the food web, as shown herein, allow investigators to infer mechanistic relationships supported by known physiological or trophic relationships, or can lead to further testable hypotheses of the relationships between trophic components. It is in this context that they are used here. As with all correlations, the variables may have a cause-and-effect relationship or both may be related to another variable.

All correlations between CUSUM plots were fit to linear models. No attempt was made to examine the fit of the relationships with a temporal offset of one variable relative to another. Refining the fit to these relationships is an ongoing effort; here the goal was to identify broad patterns. All reported CUSUM relationships herein are significant at $p < 0.0001$ unless otherwise indicated; they were not corrected for autocorrelation; all short term variance in these data were removed through the standardization calculation (transformation and summing of *z*-scores).

RESULTS

Overview

The data presentation in the following sections follows a "bottom-up" approach. Beginning with flow, then nutrients, phytoplankton, zooplankton, clams and fish, each major section starts with the changes over time, followed by their relationships with lower trophic levels and/or nutrients and flow.

Flow

The time series encompassed varying Sacramento River flows (Figure 2A). The early to mid 1980s was a period of relatively high flow and the late 1980s a period of lower flow. The early 1990s was a period of very low flow, but flow increased in the late 1990s and decreased in the early 2000s, but this latter period of low flow was not as low as in the early 1990s. The X2 metric, the isohaline where salinity is 2, is related to flow, as X2 moves inland when flow is low and seaward when flow is high (Figure 2B). Thus, the CUSUM calculations of flow and X2 are inversely related (Figures 2A,B).

Nutrients

Concentrations of NH_4^+, the dominant inorganic N form in the upper Sacramento River (station C3) and in Suisun Bay (stations D8, D7), approximately 75–80 km downstream, were lower before the mid-1980s than in later years, as evidenced in both the raw data and in the declining CUSUM trends (Figures 3A–C). NH_4^+ concentrations in the Sacramento and Suisun Bay were high in the late 1980s to early 1990s, coincident with the dry period, declined in the late 1990s, and then increased significantly after the year 2000; the upward trend in the CUSUM charts of these sites after 2000 indicates that the NH_4^+ concentrations were well above the long-term mean. In contrast to these sites, the concentrations of NH_4^+in the lower San Joaquin River have not fluctuated over the time series to the same degree, and thus the CUSUM trends for this site are different than those of stations C3, D7, or D8 (Figure 3D). The CUSUM trends for this site show no indication of increasing NH_4^+since 2000; instead, there has been a decline in these values.

The fluctuating concentrations of NH_4^+ are also are reflected in the changing NO_3^-:NH_4^+ ratio in the upper Sacramento and Suisun Bay (Figure 4). For the upper Sacramento River, the CUSUM trend increased until the mid-1980s, declined, and then increased again in the late 1990s (Figure 4A). In contrast, the CUSUM chart for this ratio for the Suisun Bay stations declined until about 1990, increased for the next several years, and then declined from 1993 onward (Figures 4B,C). The CUSUM charts of flow and the ratio of NO_3^-:NH_4^+ in the receiving waters of the upper Sacramento River revealed similar patterns (compare Figures 2A and 4A). This is interpreted to mean that under

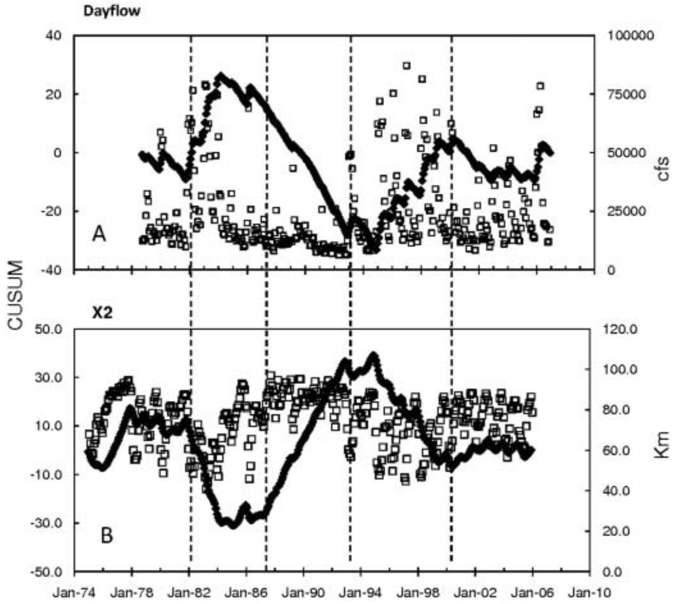

Figure 2 CUSUM values (primary axis, filled diamonds) as a function of time for (A) flow, estimated from Dayflow (see text); and (B) X2, the distance in km from the Golden Gate Bridge where the isohaline is 2. The secondary axis (open squares) for both panels gives the actual data in the units indicated. The vertical dashed lines are guides to delineate the major periods discussed in the text.

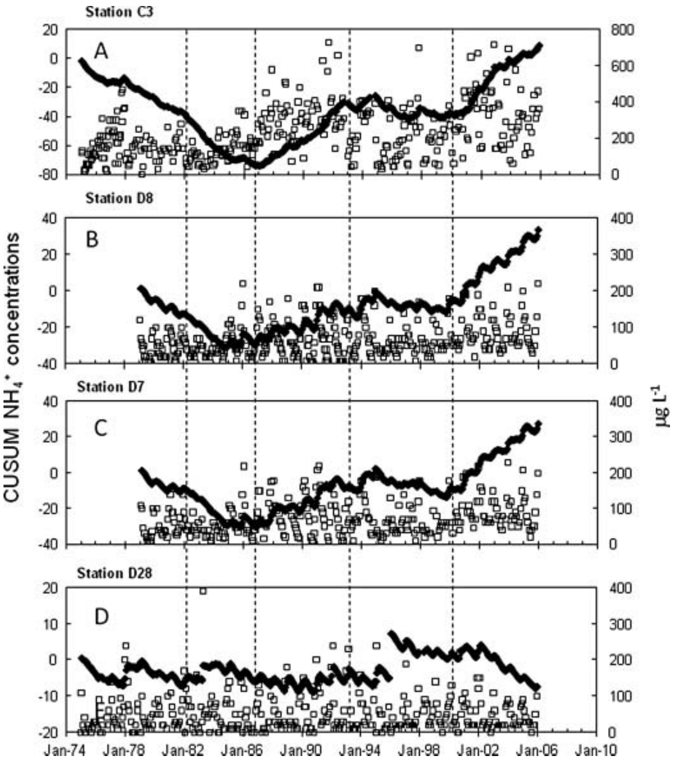

Figure 3 CUSUM values (primary axis, filled diamonds) as a function of time for ammonium (NH_4^+) concentrations for (A) the upper Sacramento at station C3; (B) and (C) Suisun Bay at stations D8 and D7; and (D) the lower San Joaquin at station D28. The secondary axis (open squares) for all panels gives the actual data in $\mu g\ L^{-1}$. The vertical dashed lines are guides to delineate the major periods discussed in the text.

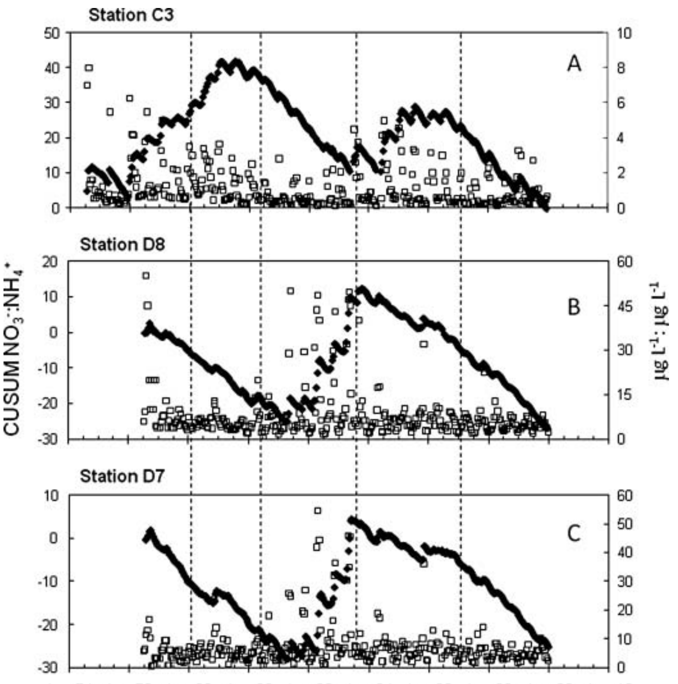

Figure 4 CUSUM values (primary axis, filled diamonds) as a function of time for the ratio of nitrate:ammonium (NO_3^-:NH_4^+) concentrations for (A) the upper Sacramento at station C3; (B) and (C) Suisun Bay at stations D8 and D7. The secondary axis (open squares) for all panels gives the actual data in $\mu g\ L^{-1}$: $\mu g\ L^{-1}$. The vertical dashed lines are guides to delineate the major periods discussed in the text.

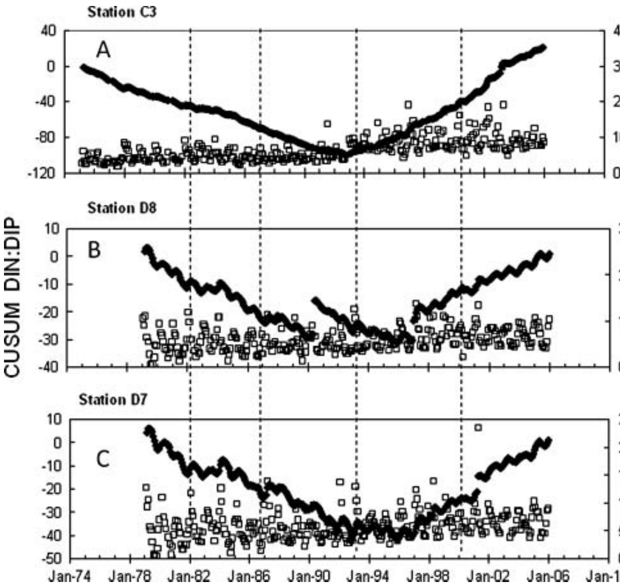

Figure 5 CUSUM values (primary axis, filled diamonds) as a function of time for the ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP) concentrations for (A) the upper Sacramento at station C3; (B) and (C) Suisun Bay at stations D8 and D7. The secondary axis (open squares) for all panels gives the actual data in μg L^{-1}: μg L^{-1}. The vertical dashed lines are guides to delineate the major periods discussed in the text.

periods of low flow, the point source discharges of NH_4^+ (see below) represented a greater fraction of the total N load in the upper Sacramento River, while under high flow there was greater dilution of the effluent NH_4^+ by other riverine nutrients (Figure 2). Under very low flow conditions (1987-1993), the ratio of NO_3^-:NH_4^+ changed to a greater degree from upstream (station C3) to Suisun Bay (stations D7 and D8; Figure 4), suggesting a greater degree of nitrification was occurring when flow was low. Although quite variable within years, the DIN:DIP ratio was below the long-term mean until the mid-1990s, when there was an increase (Figure 5).

Long-term trends in nutrient concentrations and ratios were related to changes in nutrient loading, with a major source being the Sacramento Regional wastewater treatment plant (Van Nieuwenhuyse, 2007; Jassby, 2008). The concentration of NH_4^+ discharged increased from $\sim$ 10 mg L^{-1} when the plant came on line in the early 1980s to $>$ 20 mg L^{-1} in the 2000s (Figure 6A). Concentration of NO_3^- discharged has remained $<$ 1.5 mg L^{-1}, except during the late 1990s (Figure 6B). Concentration of PO_4^{3-} in the wastewater discharge declined precipitously in the early to mid-1990s (Figure 6C), coincident with removal of P from domestic detergents by most U.S. manufacturers (Litke, 1999). Total nutrient load, a function of changing concentration and volumetric rate of discharge, also increased over time now averaging $>$500 ML day^{-1} (Figure 6D). The molar ratio of DIN:DIP of the discharge increased from $<$ 10 prior to 1994 to $>$ 20 in recent years, with few exceptions (Figure 6E). Thus, the change in DIN:DIP in the upper Sacramento River and in Suisun Bay (Figure 5) in the 1990s occurred around the same time as the DIN:DIP changed in the effluent discharge.

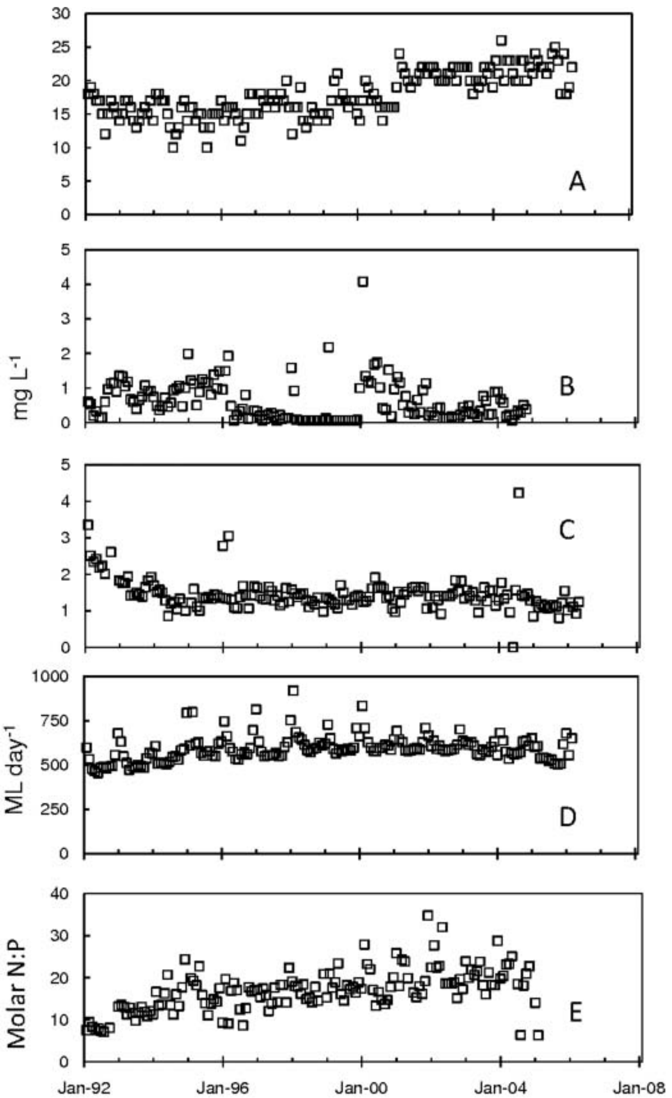

Figure 6 Nutrient concentrations (mg L^{-1}) of the wastewater effluent as a function of time for (A) NH_4^+; (B) $NO_3^- + NO_2^-$; (C) PO_4^{3-}; (D) the volumetric daily rate of effluent discharge (ML day^{-1}) from the wastewater facility; and (E) the molar ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP) for the major wastewater treatment facility in the upper Sacramento River. Although the plant came on line in 1982, the available data are only from 1992.

CUSUM trends in NH_4^+ concentration in wastewater effluent over time for the period over which such data are available (1992–2005) are highly correlated with CUSUM trends in NH_4^+concentration in the upper Sacramento River (at C3). The R^2 correlation between these trends was 0.70 ($n =$ 167 and 0.92 for the years 2000–2005 ($n = 71$, not shown) Figure 7A). Moreover, CUSUMs for NH_4^+concentration in the upper Sacramento River (at C3) were highly correlated with those in Suisun Bay (at D8; $R^2 = 0.92$, $n = 246$; Figure 7B) and at D7 ($R^2 = 0.95$, $n = 246$, data not shown) for the years since the wastewater facility began operation (1982–2005).

The correlations between flow (dayflow values) and nutrients, as total NH_4^+, NO_3^-:NH_4^+, or DIN:DIP were variable for both the upper Sacramento River and Suisun Bay (stations C3 and

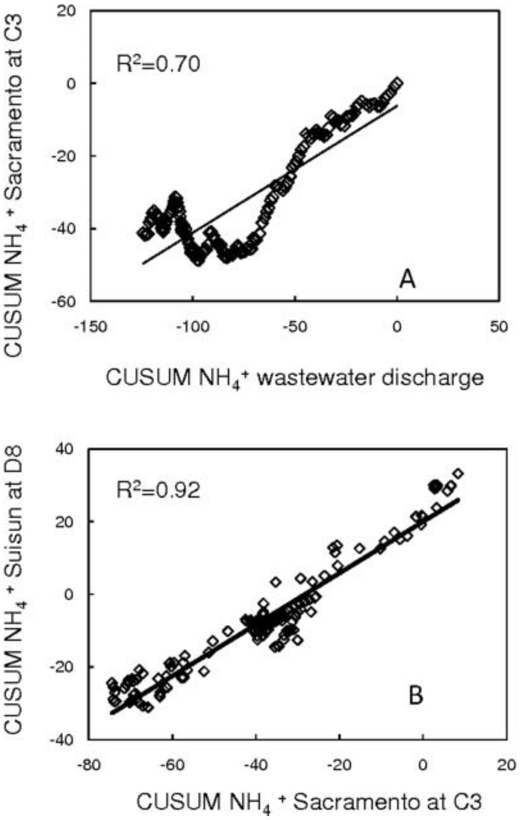

Figure 7 (A) Correlation between the CUSUM trend in NH_4^+ concentration in wastewater discharge and that in the upper Sacramento River for the period of data availability (1984–2005); and (B) Correlation between the CUSUM trend in NH_4^+ concentration in the upper Sacramento River at station C3 and that in Suisun Bay at station D8 (1984–2005).

D8) for the years since the wastewater facility began operation (Figure 8). In all cases the slope of these correlations was lower in the pre-POD years (1984–1999) than during the POD years (2000–2005). The increase in slope in the POD was related to the increase in NH_4^+ concentrations (Figure 6).

Phytoplankton

Overall phytoplankton biomass as chl *a* was high before 1987, often reaching values > 30 μg L^{-1} (Figure 9A). In 1986, these values declined abruptly, and the associated CUSUM chart has an inflection point at this time (Figure 9A). The CUSUM trend in diatoms indicates that their abundances were above the long-term population mean prior to 1982, but subsequent abundances declined to well below the long-term mean (Figure 9B). Trends in cryptophytes and green algae were opposite those of chl *a*: these algal groups were not abundant prior to 1986, increased and remained abundant until the late 1990s, and then declined (Figure 9C). Abundance of other flagellates was high in the mid to late 1980s, and again around 1996 (Figure 9D). The trend in cyanobacteria was similar to that of cryptophytes through most of the time course, first increasing in the mid 1980s when chl *a* levels were declining, but unlike cryptophytes, cyanobacteria continued to increase since 2000, a trend apparent even when the most recent increase in *M. aeruginosa* was not included (Figure 9E; Lehman et al., 2005, 2008).

When CUSUM charts of NH_4^+ concentration in Suisun Bay and those of major phytoplankton groups were compared, the correlations were all strong, but the relationship was

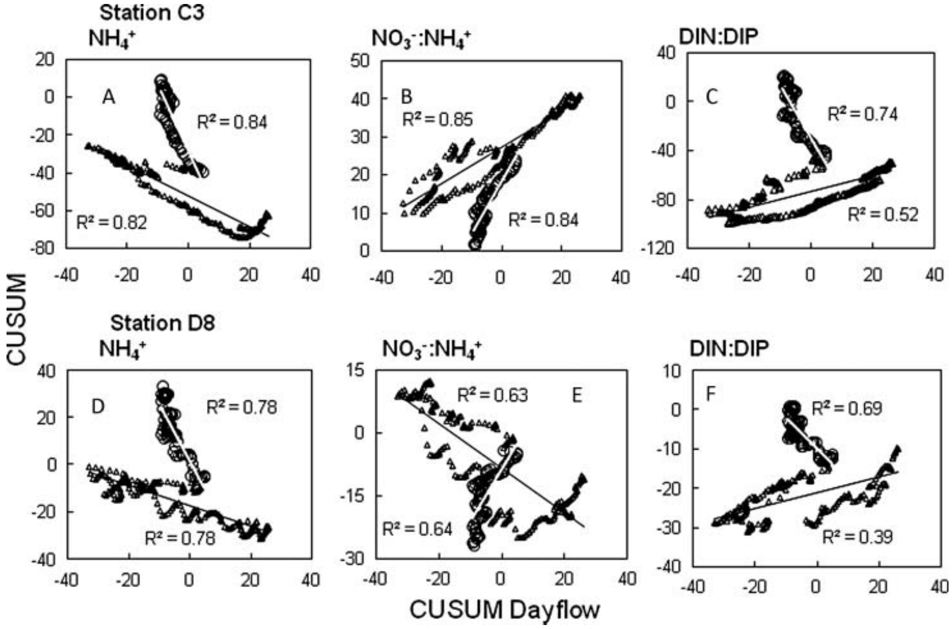

Figure 8 Correlation between the CUSUM trend in dayflow and the CUSUMS of (A) NH_4^+ at C3; (B) ratio of NO_3^-:NH_4^+ at C3; (C) ratio of DIN:DIP at C3; (D) NH_4^+ at D8; (E) ratio of NO_3^-:NH_4^+ at D8; (F) ratio of DIN:DIP at D8. All trends are for the period since the establishment of the wastewater treatment facility in the upper Sacramento (1984–2005). For each panel, the open triangles are for 1984–1999 and the closed circles are for the POD years, 2000–2005.

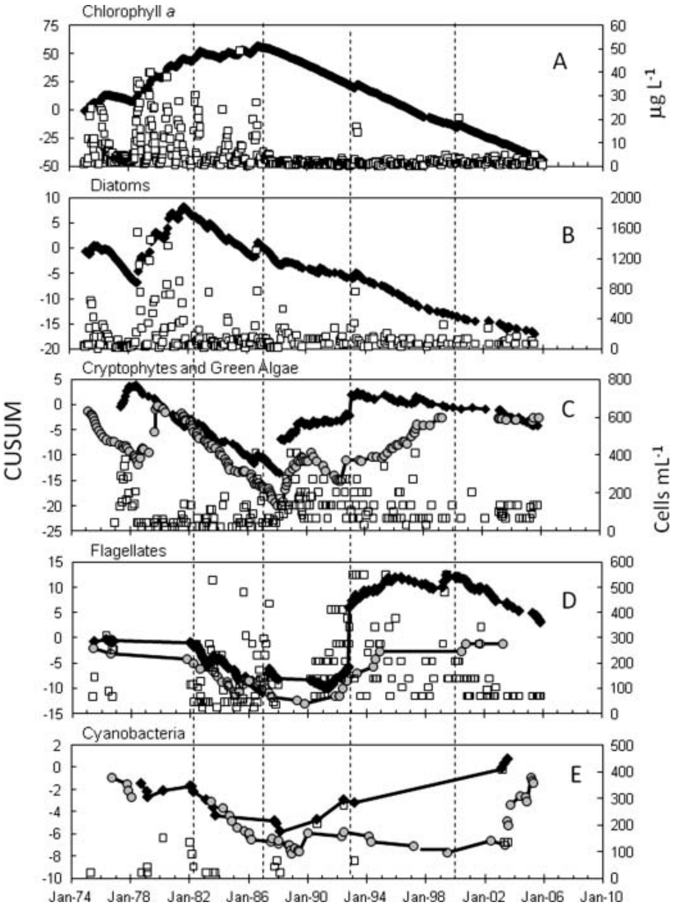

Figure 9 CUSUM values (primary axis) as a function of time for (A) total chlorophyll *a* (filled diamonds) in Suisun Bay at station D8; (B) diatom abundance (filled diamonds) at station D8; (C) cryptophytes (filled diamonds) and green algae (gray circles) at station D8; (D) total flagellates (filled diamonds) and dinoflagellates (gray circles) at station D8; and (E) cyanobacteria at station D8 (filled diamonds) and at station C3 (gray circles). The secondary axis (open squares) for all panels gives the actual data in μg L^{-1} (panel A) or in average per species cells mL^{-1} (panels B–E). Actual data for green algae (panel C), dinoflagellates (panel D), and cyanobacteria at station C3 (panel E) are not shown. The vertical dashed lines are guides to delineate the major periods discussed in the text.

negative for diatoms and positive for the other algal groups (Figure 10). When these correlations were calculated only for the years since the wastewater treatment plant has been in operation (1984–2005), they were much higher than when the entire period of record was considered. For example, for diatoms, the R^2 with CUSUM NH_4^+ increased to 0.83 ($n = 147$), that for cryptophytes increased to 0.76 ($n = 133$) and that for cyanobacteria increased to 0.97 ($n = 8$; not shown).

Copepods

The dominant copepod species also changed over time: *E. affinis* declined in 1986, and *P. forbesi* began increasing soon thereafter, and by the late 1990s, both *P. forbesi* and *L. tetraspina* were well established (Figure 11). For the entire record (1975–2005), the relationship (R^2) between the CUSUM of chl *a* and *E. affinis* is 0.93 ($n = 360$; Figure 12A). Relationships between different algal groups and copepods varied. The most pronounced were those of other flagellates and *P. forbesi* when it was dominant (1986–2000), a period for which the R^2 of their CUSUMs is 0.53 ($n = 36$; Figure 12B) and cyanobacteria and *L. tetraspina* (1988–2005), a period for which the R^2 of their CUSUMs is 0.96 ($n = 5$, $p = 0.003$; not shown).

Clams

The clam *Corbula amurensis* first appeared in significant numbers in Suisun Bay in 1987 (Figure 13). It thus appeared around the same time that the copepod *P. forbesi* began to appear (Figure 11B), and around the time that the phytoplankton assemblage had increasingly become dominated by cryptophytes and green algae (Figure 9C). Moreover, the CUSUM of NH_4^+ for Suisun Bay was highly and positively related to that of clam abundance (Figure 14A), as was the CUSUM trend in DIN:DIP (Figure 14B).

Pelagic Fish

Pelagic fish populations changed over time, coincident with changes in lower trophic levels. Delta smelt (estimated from both summer townet or FMWT indices), as well as longfin smelt, began to decline in ~ 1982 (Figures 15A,B). Within roughly a year of the start of the decline in the smelt populations, young-of-the-year striped bass also began to decline (Figure 15C).

The size of delta smelt changed over time as well, becoming smaller around 1990 (Figure 16). The timing of the change in smelt length corresponded to the time period when *P. forbesi* became established, replacing *E. affinis* as the dominant copepod (Figure 16).

In contrast, other fish species increased in numbers over the time series (Figure 17), including largemouth bass (Figure 17A), inland silversides (Figure 17B), threadfin shad (Figure 17C) and sunfish (Figure 17D). Largemouth bass and sunfish, in particular, began to increase in the POD years since 2000. Inland silversides and threadfin shad increased in the late 1990s, but subsequently decreased in the POD years.

The overall trends in these groups of fish were related to changes in their food. The CUSUM trends in delta smelt (summer townet index), longfin smelt and young-of-the-year striped bass were positively and highly correlated with CUSUM trends in *E. affinis* (Figure 18), but were negatively correlated with *P. forbesi* and *L. tetraspina* (Figure 18). The CUSUM trends in delta smelt FMWT and zooplankton were more complex than those of the summer townet, and these relationships are being developed further elsewhere and thus are not presented here. In brief, they showed a positive correlation with *P. forbesi* for the years after it became dominant, but before the POD collapse. In contrast to smelt and young-of-the-year striped bass, the CUSUM trends in largemouth bass, silversides, threadfin

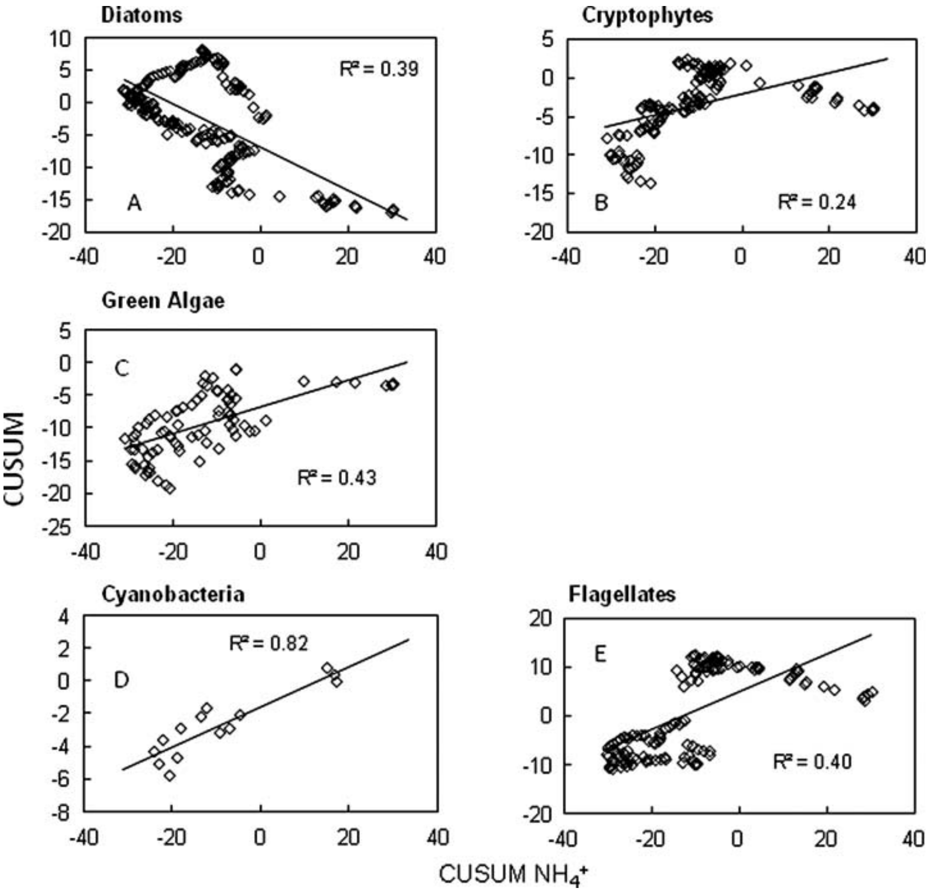

Figure 10 Correlations between the CUSUM trends in NH_4^+ and (A) diatoms; (B) cryptophytes; (C) green algae; (d) cyanobacteria; and (E) flagellates.

shad and sunfish were all negatively correlated with CUSUM trends in *E. affinis*, but were all (with the exception of largemouth bass and *P. forbesi*) positively correlated with CUSUM trends in the other copepods. Silversides, threadfin shad, and sunfish especially had very strong correlations with *L. tetraspina* (Figures 19F,I,L).

Considering that the various planktonic members of the food web were related to nutrient availability and composition, and given that the fish were related to trends in zooplankton, fish abundances were also strongly related to nutrients. CUSUM trends in delta smelt, longfin smelt and young-of-the-year striped bass were negatively correlated with CUSUM trends in NH_4^+ and in DIN:DIP (Figure 20), while CUSUM trends in largemouth bass, silversides, threadfin shad and sunfish were positively correlated with CUSUM trends in NH_4^+ and in DIN:DIP (Figure 21).

The delta smelt ultimately were related to changes in NH_4^+ of the wastewater discharge in the upper Sacramento River: The relationship between the CUSUM delta smelt summer townet index and CUSUM NH_4^+ discharge was highly significant for the entire period of record ($r^2 = 0.85$; $n = 22$; Figure 22), and near perfect for the POD years ($r^2 = 0.99$; $n = 6$, not shown).

There were no significant relationships between CUSUM trends in fish or clam abundance and the CUSUM of X2 (Table 1).

DISCUSSION

Value of the CUSUM Approach

The CUSUM approach, originally developed in 1954 (Page, 1954) is only beginning to be used in ecological time series analysis (e.g., MacNally and Hart, 1997; Breton et al., 2006; Mesnil and Petigas, 2009). It is more widely used in the manufacturing industry, as well as in public health monitoring of clinical

Table 1 Correlations between CUSUM X2, the measured distance from the Golden Gate Bridge and the isohaline where salinity is 2, and CUSUM of the fish or clam species indicated. All fish data encompass the period from 1975–2005; the clam correlations encompass the period from 1987–2005. None of these relationships were significant

Species	R^2
Delta smelt, *Hypomesus transpacificus* (summer townet index)	0.073
Delta smelt, *Hypomesus transpacificus* (fall midwater trawl index)	0.097
Longfin smelt, *Spirinchus thaleichthys*	0.167
Young-of-the-year striped bass, *Morone saxatilis*	0.037
Largemouth bass, *Micropterus salmoides*	0.089
Inland silversides, *Menidia beryllina*	0.004
Threadfin shad, *Dorosoma petenense*	0.051
Sunfish, *Lepomis* spp.	0.176

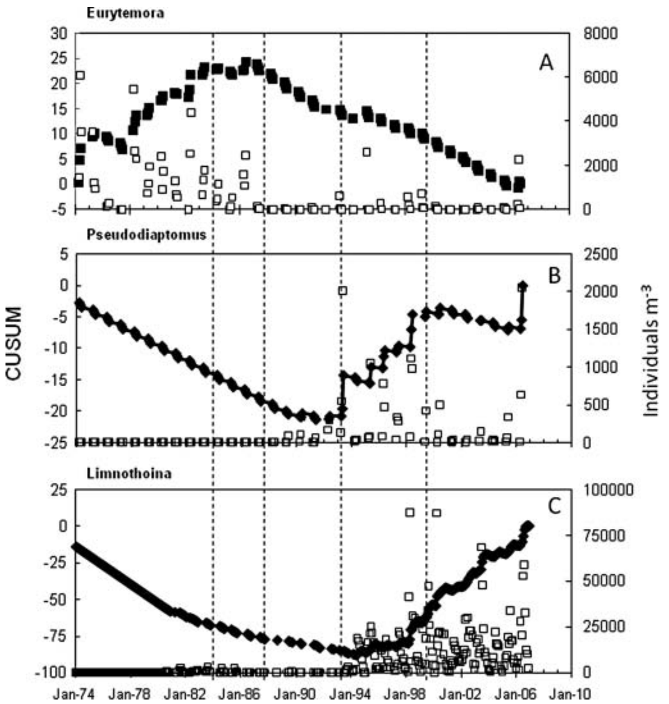

Figure 11 CUSUM values (primary axis, filled diamonds) as a function of time for the major copepods (A) *Eurytemora affinis*; (B) *Pseudodiaptomus forbesi*; and (C) *Limnoithona tetraspina* in Suisun Bay. The secondary axis (open squares) gives the actual abundance data in number of individuals m^{-3}. The vertical dashed lines are guides to delineate the major periods discussed in the text.

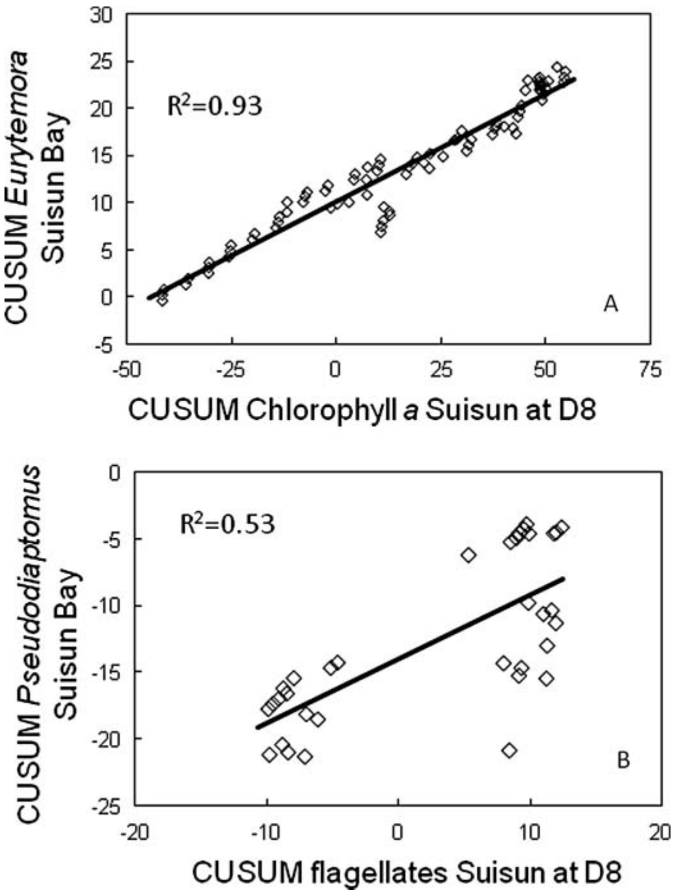

Figure 12 Correlations between the CUSUM trends in (A) chlorophyll *a* at station D8 and the copepod *Eurytemora affinis* in Suisun Bay; and (B) flagellate abundance at station D8 and the copepod *Pseudodiaptomus forbesi.*

outcomes (e.g., Sibanda and Sibanda, 2007), among other applications. It is similar to other statistical time series approaches involving examination of standard deviations of key variables (Carpenter et al., 2007). The advantages of the CUSUM approach are that it provides visually accentuated patterns making it easy to discriminate timing of shifts in variables, it is insensitive to irregularly spaced data that often occur in long-term time series where collection frequency changes over time, and *a priori* knowledge of relationships is not required, as is the case where parameterization of relationships affects complex multivariate food web models. As there is a great need for ecological models that reliably predict the composition of algal species and assemblages occurring under conditions of changing nutrient loads, the CUSUM approach may allow scientists and managers to investigate relationships and trends that previously were considered too complex to tease apart.

The CUSUM approach has recently been applied in several relevant ecological studies of long-term changes in nutrient loading and/or phytoplankton blooms in coastal lagoons or estuaries. For example, it has been applied to the long-term nutrient and plankton relationships in Florida Bay and ecosystem recovery from the effects of hurricanes (Briceño and Boyer, 2008). It has also been applied to an analysis of a 14-year (1988–2001) data set on phytoplankton in the central Belgian Coastal Zone in order to understand the relationships between nutrient loading and the North Atlantic Oscillation (NAO) and a shift in species dominance of the phytoplankton between diatoms and *Phaeocystis* (Breton et al., 2006). In the Coastal Bays of Maryland, CUSUM has been applied to understand the relationships between freshwater flow and increased nutrient loading over a period of 15 years (Glibert et al., unpub. data). Where abiotic and biotic factors are changing, often on different scales, CUSUM is a powerful approach to understand their relationships.

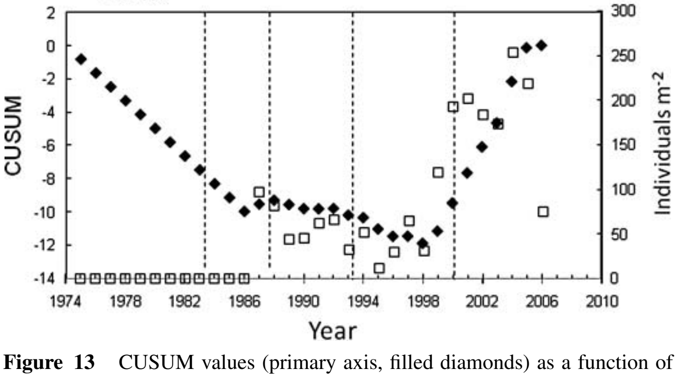

Figure 13 CUSUM values (primary axis, filled diamonds) as a function of time for the clam *Corbula amurensis.* The secondary axis (open squares) gives the actual abundance data in individuals m^{-2}. The vertical dashed lines are guides to delineate the major periods discussed in text.

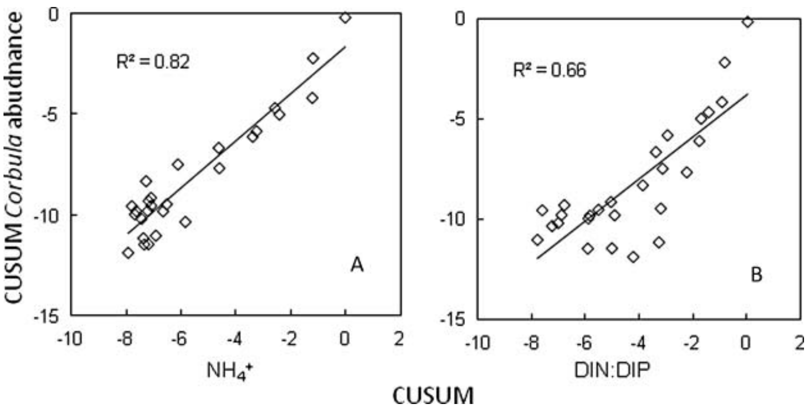

Figure 14 Correlations between the CUSUM trends in (A) NH_4^+ and (B) DIN:DIP and the abundance of the clam *Corbula amurensis.*

Nutrients as a Strong Driver of Trophic Changes Leading to Fish

Enrichment of coastal estuaries by nutrients is a function of population growth and intensified production of food and energy (Howarth et al., 2000, 2002; Smil, 2001; Cloern, 2001; Seitzinger et al., 2002; Glibert et al., 2006). Total quantity and composition of nutrients in coastal waters have changed over time (Seitzinger et al., 2002; Burkholder et al., 2006; Glibert et al., 2006), and this can lead to system changes associated with eutrophication, including hypoxia, harmful algal bloom development and loss of submerged aquatic vegetation (Nixon, 1995; Anderson et al., 2002; Glibert and Burkholder, 2006). While N and P loading have increased globally over time, N loading has increased at a rate faster than P loading in many regions (Seitzinger et al., 2002; Glibert et al., 2006; 2010), in some cases leading to expressions of eutrophication that differ from those classically considered, including inhibition of primary production by high N (Yoshiyama and Sharp, 2006). There are several reasons for the disparity in N and P loading: first, use of N fertilizers has increased faster than P fertilizers over the past several decades (Glibert et al., 2006), and, use of P in detergents has declined in the U.S. and many parts of the world (Litke, 1999). The shift in the form of N loading noted herein has also occurred in many regions throughout the world because of changes in fertilizer composition (Glibert et al., 2006). Both these changes in total N and P loading and in N form can affect food webs by altering phytoplankton species composition.

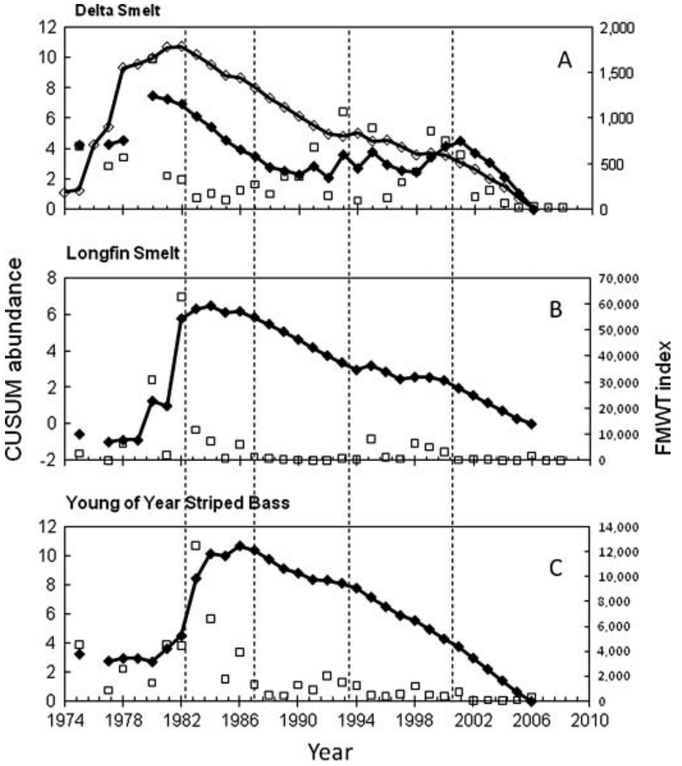

Figure 15 CUSUM values (primary axis, diamonds, triangles) as a function of time for the fish (A) delta smelt, *Hypomesus transpacificus* (fall midwater trawl-filled diamonds, summer townet-open diamonds); (B) longfin smelt, *Spirinchus thaleichthys*; and (C) young-of-the-year striped bass, *Morone saxatilis.* The secondary axis (open squares) gives the actual data based on fall midwater trawl index. The vertical dashed lines are guides to delineate the major periods discussed in the text.

This analysis has provided an evaluation of the end-to-end, inorganic nutrient-to-fish, relationships in a highly impacted, and historically nutrient-rich estuary. Numerous studies, ranging from whole lake manipulations (e.g., Mills and Chalanchuk, 1987) to oceanic food web analyses (e.g., Steele et al., 2007), have shown that alterations in nutrient loading affect trophic

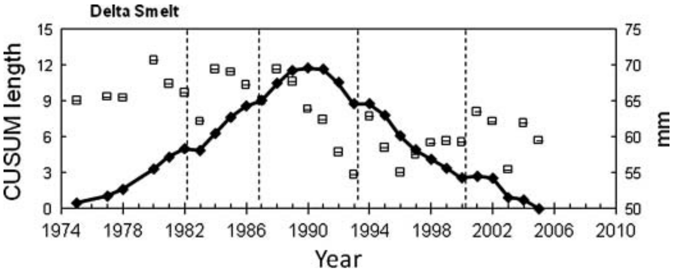

Figure 16 CUSUM values (primary axis, diamonds, triangles) as a function of time for the delta smelt, *Hypomesus transpacificus* length. The secondary axis (open squares) gives the actual data. The vertical dashed lines are guides to delineate the major periods discussed in the text.

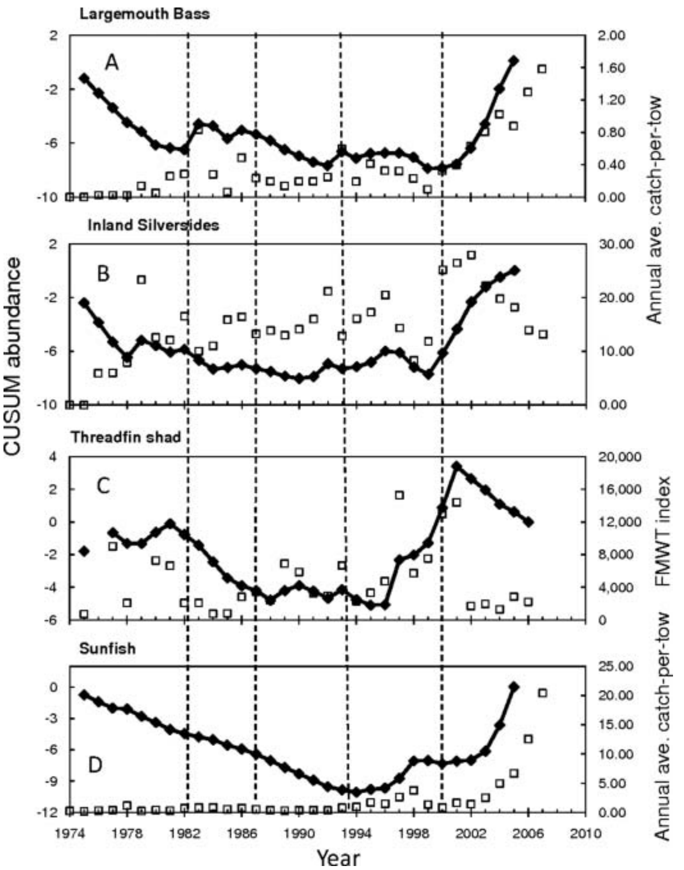

Figure 17 As for Figure 15, except for largemouth bass (*Micropterus salmoides*), inland silversides (*Menidia beryllina*), threadfin shad (*Dorosoma petenense*), and sunfish (*Lepomis* spp.). Actual data for threadfin shad are based on the FMWT index and for largemouth bass, inland silversides and sunfish are based on the annual average of catch per tow across stations regularly occupied by delta smelt.

linkages to fish. Here, evidence has been provided that such regime shifts in the San Francisco estuary correspond to periods of abrupt changes in nutrient loading. Regime shifts, fish declines and alterations in zooplankton and phytoplankton in the San Francisco Estuary have been previously described, but have heretofore been attributed to climate change (e.g., Lehman, 2004; Cloern et al., 2007), introductions of invasive species (Cohen and Carlton, 1998; Kimmerer, 2002, 2004) or other abiotic variables, such as water clarity and temperature (Feyrer et al., 2007; Nobriga and Feyrer, 2008). Understanding the factors changing this ecosystem is crucial to water management, but understanding how aquatic trophic cascades are modified by nutrients and other factors is a key scientific question and a major challenge more broadly (e.g., Carpenter and Kitchell, 1993; Polis and Strong, 1996).

The relationships shown here between nutrient composition, concentration, and dominant plankton and fish for the San Francisco Estuary can be conceptualized as 3 different major food webs over time (Figure 23): a diatom-*Eurytemora*- delta smelt period prior to 1982, a mixed phytoplankton (cryptophytes-greenalgae-flagellates)-*Pseudodiaptomus*-bass-shad period from 1982–∼2000, and a cyanobacteria-*Limnoithona*-silverside-largemouth bass-sunfish period post 2000. The availability and accessibility of long-term monitoring data at both the species-level and nutrient form-level was fundamental in this analysis.

Before 1982, chl *a* concentrations in Suisun Bay were relatively high, averaging 9 μg L^{-1}, with numerous values exceeding 30 μg L^{-1}, and diatoms, *E. affinis*, and delta smelt were all abundant. The decline in diatoms, which began in 1982, was highly correlated with the increase in NH_4^+ loading. This relationship illustrates two well known physiological processes. First, although NH_4^+ may be a preferred N form under N limitation, it can be inhibitory at high concentrations (e.g., Syrett, 1981). Second, diatoms prefer and, under some conditions, physiologically require, NO_3^- over NH_4^+, unlike many other algae which preferentially use NH_4^+ over other N forms (McCarthy et al., 1977; Syrett, 1981; Berg et al., 2001; Glibert et al., 2004, 2006). NO_3^- is used in the energy balance of these cells as a photoprotective mechanism (Lomas and Glibert, 1999a, 1999b). As NO_3^- became less available relative to NH_4^+ in Suisun Bay (Figures 4B,C), the competitive advantage shifted to phytoplankton taxa that can more efficiently use reduced forms of N. Among the phytoplankton groups that replaced diatoms in this system, cyanobacteria and many flagellates have a preference for chemically reduced forms of N (Berg et al., 2001; Glibert et al., 2004, 2006; Brown, 2010). As diatoms declined, so did *E. affinis*. Prey selectivity in zooplankton is well known; diatoms have been shown to support *E. affinis* growth and the proportion of diatoms in their diet, as well as their physiological state, affect copepod egg production and metabolism (Jones and Flynn, 2005; Ask et al., 2006).

From 1982–1986 chl *a* continued to decline, as did *E. affinis*. The virtual disappearance of chl *a* from Suisun Bay in 1987 has been attributed to the proliferation of the invasive clam, *C. amurensis*, thought to have filtration rates sufficient to remove most of the chl *a* (Kimmerer, 2002; Jassby et al., 2002). As mentioned, this exotic clam became established in Suisun Bay in ∼1986-1987, coincident with the collapse in chl *a* (Figure 13). Its increase was positively correlated with both NH_4^+ and DIN:DIP changes over time, suggesting that it thrived when the food web changed due to nutrient loading. While clams may continue to keep phytoplankton chl *a* low due to their filtering, the earlier decline in diatoms (in 1982) is better explained by the inhibitory effect of the elevated NH_4^+ loading than due to the clam invasion. Clams also have been shown to consume *E. affinis* nauplii (Kimmerer et al., 1994), but *E. affinis* was already in decline (Figure 11A) before clams became well established (Figure 13).

One of the largest changes in nutrient loading occurred in the mid 1990s when the N:P ratio roughly doubled (Figure 5). The change in N:P ratios is evident in wastewater discharge (Figure 6E), in the upper Sacramento River (Figure 5A), and in Suisun Bay (Figures 5B,C). One of the reasons for the alteration in the nutrient ratios is the reduction in P, most likely a result of the removal of P in domestic detergents (Litke, 1999). However, this was not the only change that occurred in ∼1990.

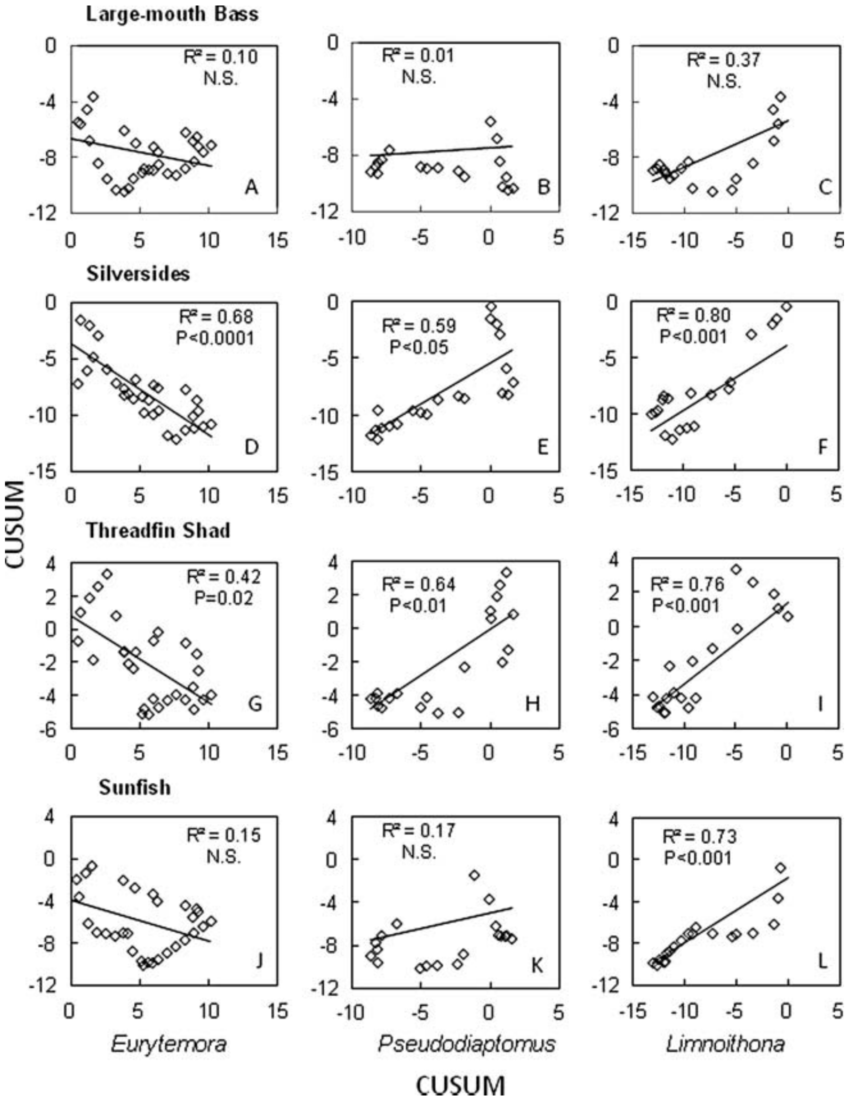

Figure 18 As for Figure 18, except for largemouth bass (panels A–C), inland silversides (panels D–F), threadfin shad (panels G–I), and sunfish (panels J–L).

Concentrations of NH_4^+ in the upper Sacramento River and throughout the estuary declined slightly (Figure 3), likely due to higher flows, leading to greater dilution of the incoming effluent. Thus, the ratio of NO_3^-:NH_4^+ increased in the upper Sacramento (Figure 4A) in the mid to late 1990s. This increase led to a very modest increase in diatoms in the upper Sacramento River (not shown), but diatoms were apparently not able to recover in Suisun Bay (Figure 9B). Their recovery likely was hampered because the DIN:DIP was higher than in the early 1980s. Instead, other flagellates proliferated (Figure 9D; Brown, 2010), and different copepod species became dominant (Figure 11). Cryptophytes and green algae were still abundant, but declined in ensuing years (Figure 9C). The copepods *P. forbesi* and *L. tetraspina* responded to an altered phytoplankton assemblage. *Pseudodiaptomus forbesi* has experimentally been shown to feed on diatoms and dinoflagellates in the laboratory (Bouley and Kimmerer, 2006). In contrast, *L. tetraspina* does poorly when feeding on diatoms (e.g., Kimmerer, 2004; Bouley and Kimmerer, 2006), and it developed after the decline in diatoms. This copepod also consumes ciliates among other food sources, but the available time series data did not allow exploration of this relationship.

Cyanobacteria began to increase in the late 1980s (Figure 9E) although, as noted above, the cyanobacterial abundances reported here are underestimated for the most recent decade (Lehman et al., 2005, 2008, 2010). Cyanobacteria thus proliferated as the DIN:DIP ratio increased (Figure 5). It has been suggested that some cyanobacteria can proliferate in low P environments when other algal classes are P-limited, due to their lower P cell quota or their ability to substitute P-containing lipids in membranes with non-P containing lipids under P limitation (Bertilsson et al., 2003; Van Mooey et al., 2009). The proliferation of cyanobacteria during the most recent decade illustrates that nutrient stoichiometry may indirectly, as well as directly, affect phytoplankton assemblagess: while cyanobacteria can tolerate elevated N:P levels, its dominance may also reflect the decline in other species without such tolerances.

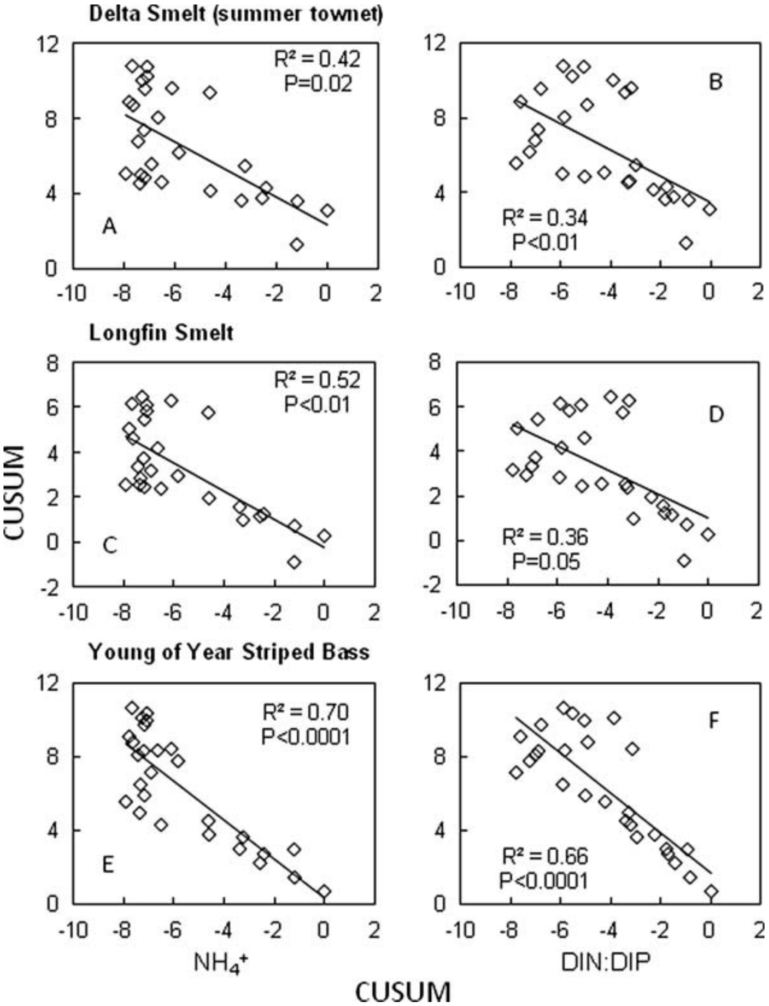

Figure 19 Correlations between the CUSUM trends in NH_4 and DIN:DIP at station D8 in Suisun Bay and CUSUM trends in delta smelt (panels A–B; summer townet index), longfin smelt (panels C–D), and young-of-the-year striped bass (panels E–F). All correlations cover the period 1975–2005.

Cyanobacteria do not have to grow faster at elevated N:P than at lower N:P values to become abundant, they merely have to grow faster than competing species groups.

Beginning in the early to mid 1980s, the ecosystem was characterized by sharp declines in delta smelt, longfin smelt, and young-of-the-year striped bass (Figure 15). And, when *P. forbesi* became established and the dominant food for delta smelt, the fish declined in size (Figure 16). As zooplankton changed, the community of fish did also, with species such as largemouth bass and silversides becoming more prevalent when *E. affinis* began its decline. While smelt is a planktivore, not all the fish studied here are, but all require zooplankton as food at least in their larval or juvenile stages or rely on prey that rely on zooplankton (Kimmerer, 2004). As predators increased, those fish that were in decline due to changes in food supply were subjected to additional stresses of predation. In the most recent decade, there were further declines in smelt, along with silversides and threadfin shad (Figure 17; e.g., Bennett, 2005; Sommer et al., 2007; Thompson et al., 2010). During this time, NH_4^+ loading from wastewater discharge increased 25%, from ∼ 9 metric tons to 12 metric tons day^{-1}(the product of Figures 6A,D), leading to a strong correlation over the time series of CUSUM trends in wastewater effluent NH_4^+ and the delta smelt (Figure 22).

The elemental composition of fish has been the subject of a considerable number of studies, from fish bioenergetics to whole system nutrient models (e.g., Kraft, 1992; Vanni, 1996; Sterner and George, 2000). Fish composition and fish size previously have been related to nutrient availability. Sterner and George (2000) speculated that the P content of fish “relates to their boniness.” Clearly there is much to be examined with regard to the ecological stoichiometry of all the components of the food web and how changes in the nutrient availability may be related not only to the food web of the San Francisco Estuary, but to the metabolism of dominant fishes as well.

Relationships of Fish Abundance with Food vs. Flow

This analysis was not intended to be a review of X2, its relationships, or the management thereof; there have been numerous

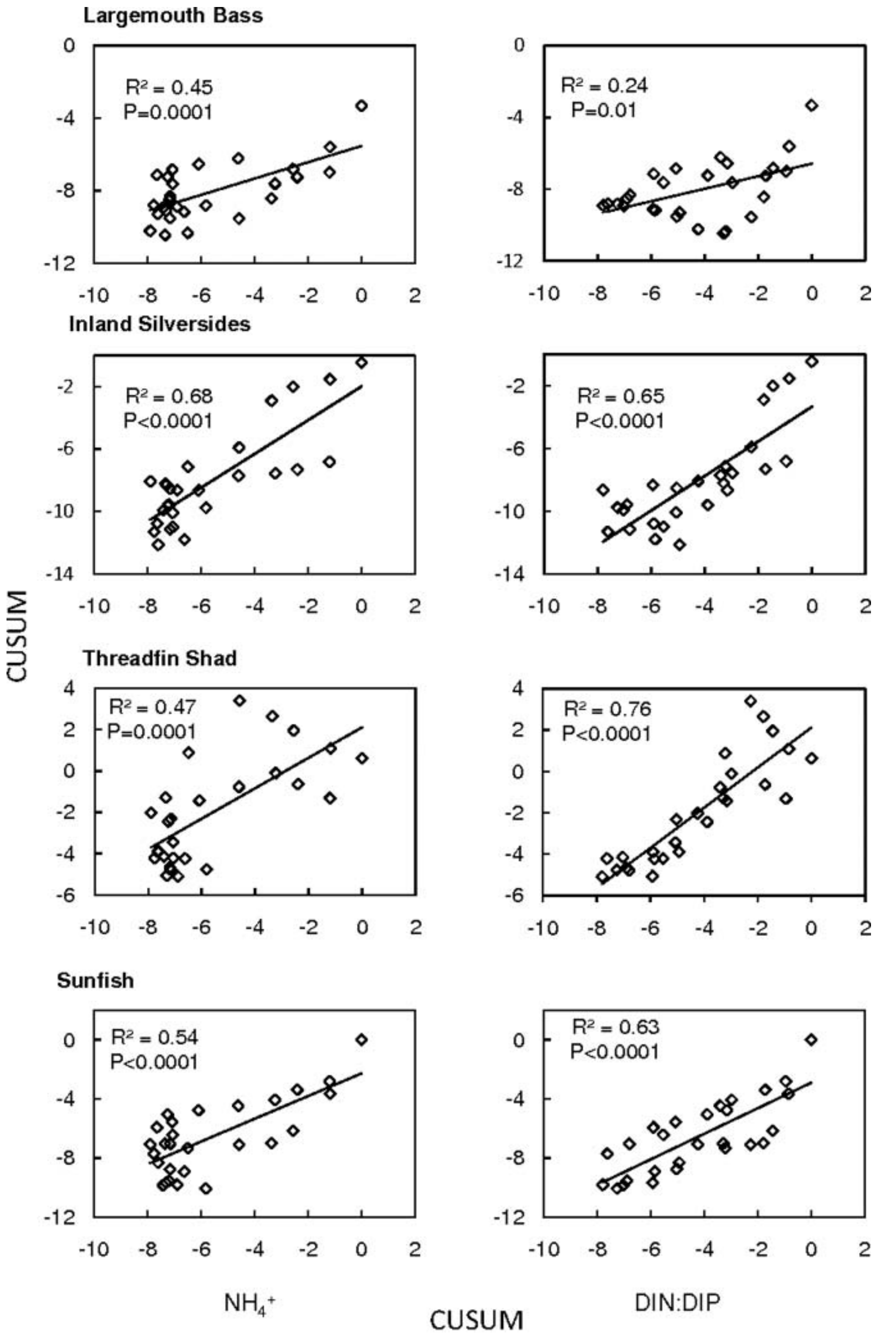

Figure 20 As for Figure 20, except for largemouth bass (panels A–B), inland silversides (panels C–D), threadfin shad (panels E–F), and sunfish (panels G–H).

other such efforts and others are ongoing. Instead, this analysis reviewed nutrients and their food web effects. The overwhelming conclusion here is the fact that relationships between nutrients and fish are stronger than those of flow and fish (comparison of Figures 20, 21, and Table 1). Furthermore, changes in flow are not correlated with all nutrients and nutrient ratios over the entire time series (Figure 8), although there were significant, but different, relationships for the pre-POD and the POD years. The slope of the relationship between CUSUM flow and nutrients changed in the POD years, coincident with the increase in effluent NH_4^+ discharge, a major driver of NH_4^+ concentrations and the nutrient ratios shown.

Nutrient Management Implications

Water management in California is challenging and contentious, and a significant fraction of the water supply for state needs is extracted from the Delta. This is done through extensive waterways and engineering projects exporting water from

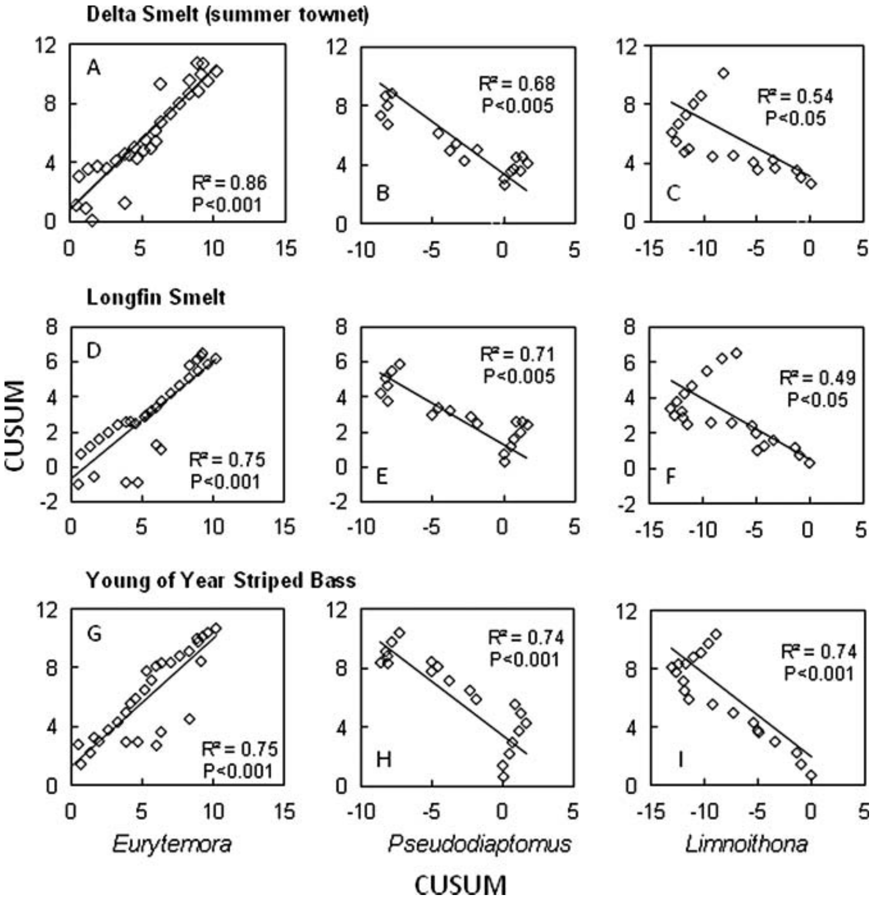

Figure 21 Correlations between the CUSUM trends in the copepods *Eurytemora affinis*, *Pseudodiaptomus forbesi* and *Limnoithona tetraspina* in Suisun Bay and CUSUM trends in delta smelt (panels A–C; summer townet index), longfin smelt (panels D–F) and young-of-the-year striped bass (panels G–I). All correlations cover the period 1975–2005 for *E. affinis*, and 1987–2005 for the other copepods.

the Delta, via pumps and aqueducts, to the southern, drier, part of the state (Brown et al., 2009). In recent years, restrictions in water use have been mandated through federal court decisions because of declines in delta smelt abundance and its listing as a threatened and/or endangered species (Wanger, 2007a, 2007b). Water restrictions are thought to be required to reduce further loss of these fish by entrainment in export pumps. However, management strategies to date have not reversed fish declines because they have not addressed the ultimate cause of the change at the base of the food web and the complex role of nutrient form and quantity. When food web analyses are not linked to ultimate causes of change, management guidance is inconclusive, as in the MacNally et al. (2010) multivariate analysis of fish decline in the Delta. MacNally et al. (2010) stated, "The relatively large proportions of variance explained by interactions among the declining fishes and their prey suggest that trophic interactions also are important, but it is less clear how management actions could modify such relationships."

The present study supports the premise that reduction of the NH_4^+ effluent into the Bay Delta is essential to restoring historic pelagic fish populations and that until such reductions occur, other measures, including regulation of water pumping or manipulations of salinity, as has been the current strategy, will likely show little beneficial effect. By altering nutrient composition and nutrient load, it is likely that a healthy phytoplankton assemblage including diatoms could be restored. A clear man-

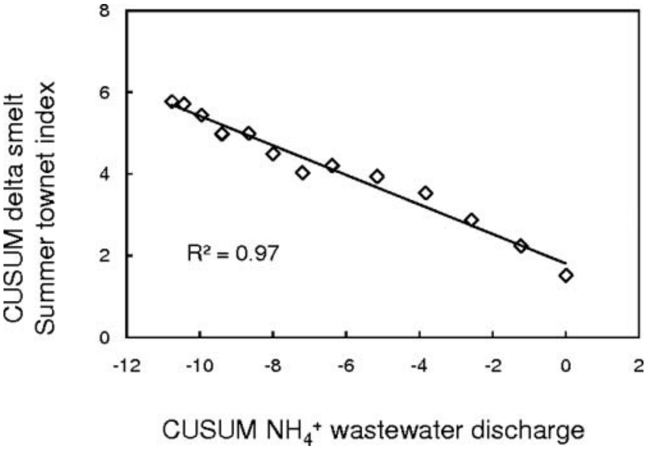

Figure 22 Correlation between the trend in CUSUM in ammonium concentration in wastewater discharge in the upper Sacramento River and the trend in CUSUM delta smelt, estimated from the summer townet index.

agement path is the application of nitrification and denitrification processing of the dominant nutrient source, the wastewater effluent, prior to discharge into the estuary to (1) decrease NH_4^+ concentration in the river; (2) reduce N:P ratio of the effluent; and (3) increase NO_3^-:NH_4^+ ratio to a level required to increase diatom abundance to support a more favorable food web for fish production (Figure 22). Pre-1982 nutrient concentrations and ratios could serve as a management target. Historic data can serve as the "reference condition" to establish numeric nutrient criteria when, as is the case here, there is knowledge of how the system functioned prior to the nutrient loading impacts (U.S. EPA, 2001, 2010).

The findings herein point to an important consideration in the development of numeric criteria for nutrients in estuaries, a challenge that many states are now facing (U.S. EPA, 2010; Glibert, 2010). Many such criteria, or integrated indices of water quality status and trends, are based on total N or P, rather than specific forms of N or P (U.S. EPA, 2010). These findings show that nutrient form is related to the "quality" of phytoplankton. Thus, nutrient forms or ratios should be considered in criteria development if effects on food webs are to be related to such criteria.

Prior studies in the Bay Delta suggested that phytoplankton assemblage composition and total phytoplankton biomass were related to NH_4^+ availability or dissolved inorganic N:P ratios (Wilkerson et al., 2006; Dugdale et al., 2007; Van Nieuwenhuyse, 2007). However, there have been no prior efforts linking these changes through the food web. In fact, the suggestion that nutrient loading (particularly NH_4^+) affects the food web was discounted because it was assumed that NH_4^+ is a preferred form of N for phytoplankton uptake (of all species), and in order to have effects on higher trophic levels, the levels must be in the range causing direct toxicity. The pH of the receiving waters prevents formation of the toxic NH_3, and NH_4^+ levels are generally below levels considered by the U.S. Environmental Protection Agency criteria for fish habitat (McCarthy et al., 1977; Millero, 2006; U.S. EPA, 2009). The latter treats NH_4^+ as a toxicant. The more subtle ecological impacts of NH_4^+ loading and the importance of changes in NO_3^-:NH_4^+ in phytoplankton succession have not been appreciated. Moreover, the potential for P limitation (Van Nieuwenhuyse, 2007) has not been given full consideration because the concentrations are not at levels normally taken to be indicative of limitation, i.e., less than the half saturation constant for uptake (e.g. Reynolds, 2006; Jassby, 2008). The analysis herein reconciles the seeming inconsistencies of the nutrient regulation hypotheses advanced by Wilkerson et al. (2006) and Dugdale et al. (2007) and by Van Nieuwenhuyse (2007). While Wilkerson et al. (2006) and Dugdale et al. (2007) have suggested that the controlling nutrient is N, especially NH_4^+ inhibition, Van Nieuwenhuyse (2007) suggested that P limitation was limiting to phytoplankton. From the analysis here, it appears that both have had significant effects on phytoplankton communities, but their major effects have occurred at different points along the time course.

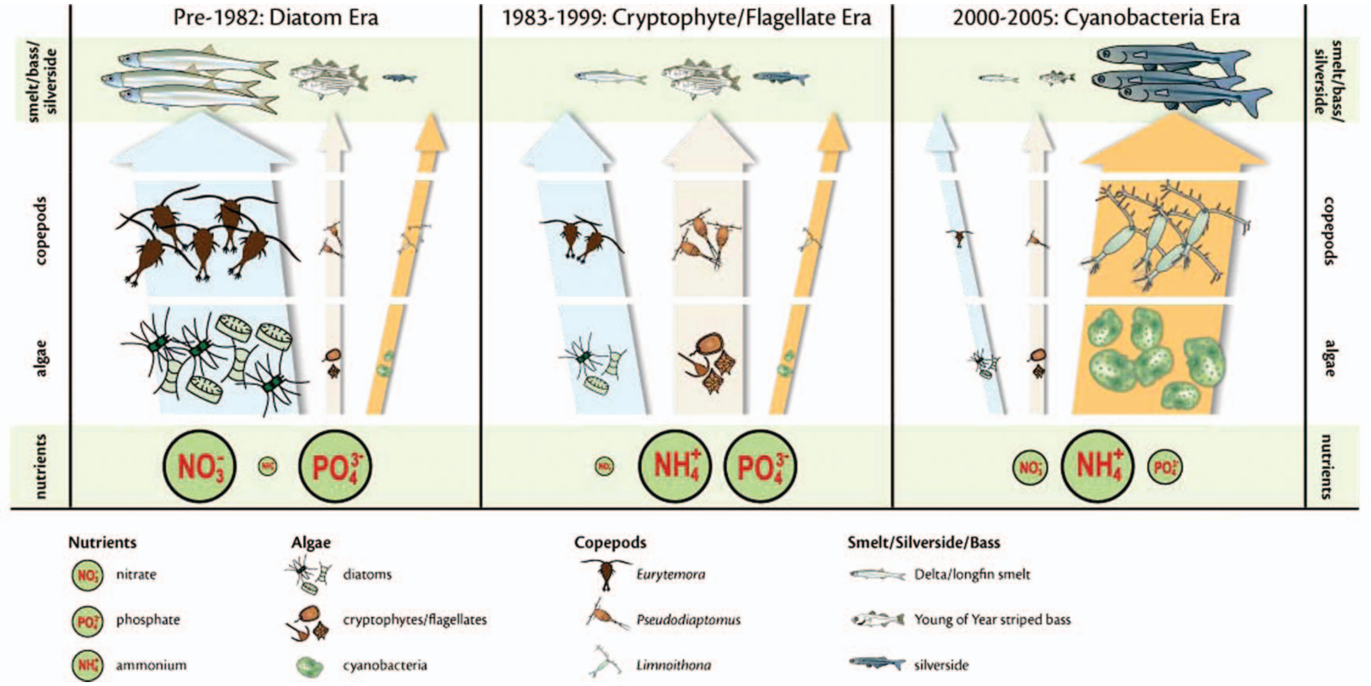

Figure 23 Conceptual diagram of some of the hypothesized changes in the food chain from phytoplankton to fish that have occurred in the Sacramento-San Joaquin Estuary over the past 30 years. Each of these hypothesized food chains has different dominant nitrogen forms or amounts relative to phosphorus. This conceptual model is intended simply to highlight some of the major flows of energy and materials and does not include all organisms, pathways or flows. The size of the symbols is meant to infer relative importance.

The changes in food web structure with changes in nutrient form and/or nutrient ratio suggest that the Eppley and Peterson (1979) paradigm applies in this nutrient rich estuary. That paradigm, which suggests that NO_3^--based food webs are fundamentally different from those of NH_4^+-based food webs, was originally developed for oligotrophic, oceanic waters. Here, as in the oceanic condition, NO_3^--based food webs were supported by higher proportions of diatoms and the NH_4^+-based food webs were supported by higher proportions of flagellates, cryptophytes and cyanobacteria. Both food webs supported fish, although different species.

The analysis described here should be highly relevant to other systems that have been subject to alterations in N and P loading and N form. The fact that chl *a* declined over time as N loading increased has deflected management attention away from nutrients. It is counterintuitive to the normal progression of eutrophication, typically resulting in higher algal biomass and a shift from benthic to pelagic production (Cloern, 2001). The inhibitory effect of NH_4^+ on diatoms seen here has, however, been observed in other estuaries, such as the Delaware Estuary and the inner bay of Hong Kong Harbor (Yoshiyama and Sharp, 2006; Xu et al., 2010). In the Delaware Estuary, inhibition by NH_4^+ was greatest in the colder months, when diatoms dominated (Yoshiyama and Sharp, 2006). From a management perspective, not only is near-field alteration of phytoplankton growth important, but so too is the potential for large downstream impacts - impacts not often associated with discharges far removed in space. In this study, CUSUM trends in discharge of NH_4^+ from the treatment plant were highly related to those of NH_4^+ concentrations far downstream, $\sim$ 80 km from the treatment plant (Figure 7). The Sacramento River acted as a conduit for transport of N downstream.

Supporting the idea that correct balance of nutrients is important for restoration of delta smelt and other pelagic fish, there is a small but apparently successful subpopulation of delta smelt in a restored habitat, Liberty Island. Liberty Island is outside the immediate influence of Sacramento River nutrients. It has abundant diatoms among a mixed phytoplankton assemblage, as well as lower NH_4^+ levels and higher ratios of $NO_3^-:NH_4^+$ than the main Sacramento River (Lehman et al., 2009). Thus, if efforts are made to restore additional habitat, consideration should be given to location of the habitat to be restored relative to the main sources of nutrients. This system demonstrates that alterations in nutrient forms do indeed alter food webs, even when all major nutrients are abundant, as was the case prior to 1994, or when one nutrient (in this case P) is controlled, as is the current condition in the upper Sacramento River. Additionally, nutrients that are abundant when one nutrient is controlled can be displaced in space, having significant effects on the ecology and food chain downstream. The CUSUM approach was an effective, sensitive, simple means to detect these relationships. These relationships also lead to directly testable hypotheses and experiments that can further understanding about the role of changing nutrient loads and composition on the dynamics of the food web in this system.

SUMMARY

Nutrient changes in concentration and form in the San Francisco Estuary and Bay Delta are significantly correlated with changes in components of the food web over time. These changes are highly related to loadings from a single major point source. The long-term changes in NH_4^+, the dominant N form that is discharged from the Sacramento River effluent plant are similar in the upper Sacramento River (C3) and 80 km in Suisun Bay (D8 and D7). However, they are not similar in lower San Joaquin River (D28), consistent with previous findings that inflow from the Sacramento River and its chemical constituents dominate over those of the San Joaquin. Changes in nutrient loadings and forms were related to changes in the phytoplankton assemblage, which in turn were related to changes in zooplankton, and in turn, related to clam abundance, and to the abundance of various fish species. The invasive copepods *P. forbesi* and *L. tetraspina* became dominant when the phytoplankton community shifted from diatom to flagellate and cyanobacterial dominance. Fish species fell into two groups: those that were positively correlated with trends in abundance of *E. affinis* and negatively correlated with *P. forbesi* and *L. tetraspina*, and those that were negatively correlated with *E. affinis* and positively correlated with *P. forbesi* and *L. tetraspina*. Trends in the former group of fish also were related negatively to trends in NH_4^+ and DIN:DIP, while the opposite pattern emerged for the latter group of fish species. Trends in abundance of the clam, *C. amurensis*, were also highly related to trends in NH_4^+ and DIN:DIP, suggesting that this invasive species was opportunistically responding to a change in ambient conditions when it proliferated. All of these relationships were significantly more robust than relationships with flow or X2; there were no significant relationships between the CUSUMs of X2 and nutrients, phytoplankton species, zooplankton or fish. Thus, a clear management strategy is the regulation of effluent N discharge through nitrification and denitrification. Until such reductions occur, other measures, including regulation of water pumping or manipulations of salinity, as has been the current strategy, will likely show little beneficial effect. Without such action, the recovery of the endangered pelagic fish species is unlikely at best.

ACKNOWLEDGMENTS

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Ecological Stoichiometry, Biogeochemical Cycling, Invasive Species, and Aquatic Food Webs: San Francisco Estuary and Comparative Systems

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Eutrophication has altered food webs across aquatic systems, but effects of nutrient stoichiometry (varying nutrient ratios) on ecosystem structure and function have received less attention. A prevailing assumption has been that nutrients are not ecologically relevant unless concentrations are limiting to phytoplankton. However, changes in nutrient stoichiometry fundamentally affect food quality at all levels of the food web. Here, 30-year records of nitrogen and phosphorus concentrations and ratios, phytoplankton, zooplankton, macroinvertebrates, and fish in the San Francisco Estuary (Bay Delta) were examined to collectively interpret ecosystem changes within the framework of ecological stoichiometry. Changes in nutrient concentrations and nutrient ratios over time fundamentally affect biogeochemical nutrient dynamics that can lead to conditions conducive to invasions of rooted macrophytes and bivalve molluscs, and the harmful cyanobacterium Microcystis. *Several other aquatic ecosystems considered here have exhibited similar changes in food webs linked to stoichiometric changes. Nutrient stoichiometry is thus suggested to be a significant driver of food webs in the Bay Delta by altering food quality and biogeochemical dynamics. Since nitrogen-to-phosphorus ratios have increased over time, an overall implication is that remediation of fish populations in the San Francisco Estuary will require significant nitrogen reductions to restore the historic ecological stoichiometric balance and the food web.*

Keywords ammonium, Bay Delta, *Corbula amurensis*, delta smelt, *Egeria densa*, *Microcystis*, nitrogen, nutrient ratios, pelagic organism decline, pH effects, phosphorus, stoichiotrophic imbalance

INTRODUCTION

This review integrates concepts of eutrophication (e.g., Nixon, 1995; Cloern, 2001; Wetzel, 2001), ecological stoichiometry (Sterner and Elser, 2002), and stable state theory (Scheffer et al., 1993) in an overall framework for evaluating the extent to which long-term changes in aquatic food webs in the San Francisco Bay Delta and other aquatic ecosystems have resulted from human-driven changes in nutrient loads and forms. Eutrophication is the process whereby systems are enriched with nutrients with various deleterious effects, whereas ecological stoichiometry—consideration of nutrient ratios—relates changes in the relative elemental (e.g., nitrogen [N], phosphorus [P], and carbon [C]) composition in body tissue and the water column. Stable state theory suggests that external drivers or disturbances (here, nutrients) can shift a system from one stable state to another via interacting feedbacks.

Nutrient ratios have often been used to infer system limitation when concentrations are known to be limiting to the phytoplankton assemblage (Reynolds, 1999; Downing et al.,

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2001). A prevailing view has considered nutrient ratios to be ecologically irrelevant unless concentrations are limiting to phytoplankton growth rate. Such a narrow application of nutrient ratios, conferring importance only when concentrations limit phytoplankton growth rate, needs to be expanded in recognition of that fact that changes in nutrient stoichiometry fundamentally affect *food quality*—from the base to the apex of aquatic food webs—as well as system *biogeochemistry*, whether nutrients are limiting or not (Sterner and Elser, 2002).

The central premise of this article is that alterations in nutrient stoichiometry have profound consequences for aquatic food webs resulting from different organismal needs for different nutrients and different abilities to sequester nutrients, and that biogeochemical feedbacks associated with species assemblage changes may shift systems to new stable states. In this review, 30 years of records of inorganic N and P concentrations, phytoplankton, zooplankton, invertebrates, and fish in the San Francisco Estuary were examined to interpret ecosystem changes within the conceptual framework of nutrient dynamics. The questions addressed in this article are: *To what extent do ecosystems self-assemble as a function of nutrient stoichiometry? Does changing nutrient stoichiometry have ecosystem effects even when nutrients are not at levels normally taken to be limiting by primary producers? If the food web changes that have occurred are related to nutrient loads, what are the biological, physiological, or biogeochemical processes that help to explain, mechanistically, why such food web changes may have occurred?* And, *what are the management implications of such relationships?*

These questions are highly relevant to the issue of cultural eutrophication, which is one of the most pressing problems affecting both coastal and freshwater ecosystems worldwide (e.g., Vitousek et al., 1997a,b; Howarth et al., 2002; Galloway and Cowling, 2002; Turner et al., 2003; Conley et al., 2009; Doney, 2010). Nutrient pollution is on the rise because of dramatic increases in human population in many regions, and concomitant increasing demands for energy, increases in N and P fertilizer use for agriculture, changes in diet that are leading to more meat production and animal waste, and expanding aquaculture industries (e.g., Smil, 2001; Galloway and Cowling, 2002; Galloway et al., 2002; Howarth et al., 2002; Glibert et al., 2010). Although eutrophication is occurring globally, nutrient exports from coastal watersheds are not evenly distributed (Seitzinger et al., 2002a, 2005; Howarth et al., 2005; Glibert et al., 2006a, 2010), nor is the export of N and P changing proportionately. Much remains to be understood about the implications of changes in N:P supplies, globally and regionally for aquatic food webs. Differentiating food web changes due to changes in nutrient loads from those due to stochastic events has important implications for restoration and management. A major management implication stressed here is the importance of co-management of N and P. A common practice has been to reduce P in point sources without concomitant reductions in N while overlooking the fact that nutrient loading results in large sediment deposits of nutrients that influence the overall system for an extended period (years) after loading rates are reduced. Reductions in anthropogenic P loads can initially result in a decline in phytoplankton biomass, but the sediment "pump" of stored P replenishes P supplies in the water column, promoting benthic productivity, which, in turn, has multiple effects on the food web. If the system additionally receives N, especially in the form of ammonium (NH_4^+), it can be expected to shift to undesirable dominant species among primary producers, with ramifications extending to higher trophic levels.

Nutrient enrichment interacts with aquatic food web dynamics in complex ways. At the planktonic level, many of these changes are well understood for phytoplankton. With nutrient enrichment, biomass may increase without a change in the proportion of the dominant planktonic organisms, but, more commonly, as nutrients continue to increase, a shift in plankton assemblage composition is observed, with large diatoms giving way to smaller phototrophs, such as cyanobacteria and various flagellates (e.g., Smayda 1989; Marshall et al., 2003; MacIntyre et al., 2004; Finkel et al., 2010). Many of these species can be harmful to higher trophic levels, disrupting normal ecosystem function. The dominance of such species can result in a failure of normal predator–prey interactions, which, in turn, enhances the transfer of nutrients that sustain the harmful algal blooms at the expense of competing algal species (Irigoien et al., 2005; Mitra and Flynn, 2006; Sunda et al., 2006). Such changes have ramifications at all levels of the food web. Increased phytoplankton and macroalgal proliferations at high nutrient levels affect seagrasses and benthic microalgae that compete for light (Harlin, 1993; Deegan, 2002; Burkholder et al., 2007), altering the food web structure by changing the habitat needed to support fish and shellfish. Fundamentally, all aspects of metabolism, predator–prey interactions, and species success are altered when a system is stressed by nutrient over-enrichment (Breitburg et al., 1999; Breitburg 2002).

Adding to the complexity of understanding system and food web changes due to increased nutrients is the relatively recent phenomenon of changing stoichiometry of nutrient supplies. In many parts of the developed world, P reductions have been undertaken (e.g., in sewage effluents and laundry detergents), as a means to reduce or control algal blooms whereas N loads often are allowed to remain elevated (Glennie et al., 2002; European Environment Agency, 2005). Thus, not only have many systems undergone eutrophication, but many are showing signs of reversal due to this single nutrient reduction. Nevertheless, even when many eutrophication symptoms are reduced, such as hypoxia and algal blooms, the systems only appear to partially recover (Burkholder, 2001; Burkholder and Glibert, 2011); their food webs do not appear to return to their pre-eutrophic state.

The San Francisco Estuary, or Bay Delta, California, USA (Figure 1) is an ideal ecosystem for addressing the questions posed above. The Bay Delta is one of the largest estuarine systems on the U.S. Pacific coast, as well as one of the nation's largest managed and engineered water systems. It is the largest source of municipal and agricultural fresh water in California and is home to economically important

Figure 1 Map of the San Francisco Estuary and the Sacramento–San Joaquin Bay Delta. The region outlined in the box represents the region where virtually all of the stations examined in this article were located. The diamond indicates the Sacremento Regional Wastewater Treatment site. Stations D4–D8 represent the stations where water chemistry data were used for this analysis (color figure available online).

fisheries. From phytoplankton to fish, the food web of this system has changed significantly over the past several decades (Alpine and Cloern, 1992; Jassby et al., 2002; Kimmerer, 2004, Kimmerer et al., 2010; Jassby, 2008). The Bay Delta has been extensively monitored for most biological constituents since the 1970s, so this is a system rich in data with which to explore these relationships. It has also been influenced by major changes in nutrient loads and nutrient composition (e.g., Van Nieuwenhuyse, 2007; Dugdale et al., 2007; Jassby, 2008; Glibert, 2010). N loads have increased substantially since the mid-1980s, while P loads increased and then declined in the mid-1990s to levels that approximate earlier conditions.

The Bay Delta is an inverse delta and receives the majority of its flow from the Sacramento and San Joaquin Rivers (Atwater et al., 1979; Nichols et al., 1986). The Sacramento River is the larger river, contributing ~80% of the freshwater to the system (Jassby, 2008). The upper reaches drain 61,721 km^2, while the upper San Joaquin River drains 19,030 km^2 (Sobota et al., 2009). Major modifications to the Bay Delta have occurred over the past century, including drainage of marshes to support agriculture, installation of dikes to prevent farmland flooding, expansion and deepening of shipping lanes, and significant diversion of water to various users throughout the state (Atwater et al., 1979). The Sacramento and San Joaquin Rivers converge at the confluence of the delta, then flow into Suisun Bay, San Pablo Bay, flow ultimately into the Central and South Bays. River flow has varied about ten-fold in the past decades due to the effects of prolonged droughts and El Niño – Southern Oscillation wet years (Jassby, 2008).

The Bay Delta ecosystem has also been significantly modified by invasive species, including clams, bay grasses, various species of copepods, and fish over the past several decades (Carlton et al., 1990; Cohen and Carlton, 1995, 1998; Kimmerer, 2002). In fact, this system has been characterized as one of the most heavily invaded estuaries in the world (Cohen and Carlton, 1995, 1998), with most of these invasions traced to increased trading with Asia and "discharge of ballast water, inadvertent or deliberate release of aquarium organisms, deliberate introduction for fisheries, and inadvertent release of bait organisms" (Kimmerer, 2004, p. 8; National Research Council of the National Academies [NRC], 2010; Winder et al., 2011). The Bay Delta has been used as an example of a system undergoing "invasion meltdown," implying that frequent invasions alter habitat and promote additional invasions (Simberloff and Von Holle, 1999; Simberloff, 2006), perhaps to the "point of no return." The extent to which habitat changes related to nutrient enrichment have contributed to these successful invasions or other food web changes in the Bay Delta has not been explored, because it was earlier concluded that nutrients were in excess of phytoplankton demand and therefore not regulating (Alpine and Cloern, 1992; Cloern and Dufford, 2005).

The fundamental question of whether changes in the food web are a result of anthropogenic changes, especially changes in nutrient loads and balance, or whether they are the result of stochastic events, has more than academic relevance. Many management questions and actions are directly affected by the extent to which the factors contributing to the food web changes can be identified and managed. Several fish, including the delta smelt (*Hypomesus transpacificus*) and longfin smelt (*Spirinchus thaleichthys*), are on the Federal Endangered Species List or are considered threatened (Wanger, 2007a,b). Water exports have been restricted by court order in recent years in an attempt to restore these species; new habitat is being created with the hope that it will contribute positively to the restoration of the system; and major re-engineering of the flow is also being debated for the coming decades (e.g., Bay Delta Conservation Plan, 2010, http://baydeltaconservationplan.com/BDCPPlanningProcess/ReadDraftPlan/ReadDraftPlan_copy1.aspx). Costs of these efforts are estimated in the hundreds of millions to billions of dollars.

Despite current management efforts, delta smelt have undergone further significant population declines in the past decade, along with longfin smelt, threadfin shad (*Dorosoma petenense*), and young-of-the-year striped bass (*Morone saxatilis*; Rosenfield and Baxter, 2007; Sommer et al., 2007; Baxter et al. 2010). Accelerated losses during the past decade have been termed the pelagic organism decline (POD) (Sommer et al., 2007; Baxter et al. 2010). Much of the debate about the declines in fish populations have been centered on the effect of the export pumps that supply the water to large aqueducts that transport it throughout the state for municipal and agricultural use.

The complexity of the Bay Delta system—hydrologically and ecologically—cannot be underestimated. Kimmerer (2004, p. 12) noted that "complex environments such as estuaries often seem not to obey general rules, but to respond in specific ways for which the general literature on estuaries provides little guidance." The frequent changes, invasions, and effects of engineering and other management actions complicate these relationships. This article focuses on nutrient issues that heretofore, for the most part, have not been emphasized, and it suggests some general rules by which aquatic ecosystems may respond. This article develops the hypothesis that nutrient changes underlie this complexity. While there have been multiple freshwater systems to which ecological stoichiometric (Sterner and Elser, 2002) and stable state principles (Scheffer et al., 1993) have been applied (described in more detail throughout this article), there have been relatively few examples where these principles have been applied to estuaries. Recent evidence suggests that the changes in trophodynamics in the Bay Delta system may be related to nutrient changes (e.g., Wilkerson et al., 2006; Dugdale et al., 2007; Van Nieuwenhuyse, 2007; Glibert, 2010). However, ecosystem changes have not been collectively interpreted in the conceptual framework of nutrient dynamics. The multiple stressors on fish and the aquatic system in general have been, and are, the subject of multiple working groups, panels, and a National Academy Study (NRC, 2010) as the management implications are far reaching.

This article is written in six parts, bringing to bear the ecological principles of eutrophication (sensu Nixon, 1995; Cloern, 2001), ecological stoichiometry (sensu Sterner and Elser, 2002), and alternative state theory (sensu Scheffer et al., 1993). Part I outlines the conceptual overviews of eutrophication, elemental stoichiometry, nutrient ratios, and alternative stable states and their inter-relations. Part II probes the long-term nutrient and organismal changes in the Bay Delta and their ecological stoichiometric relationships, beginning with phytoplankton, then zooplankton, macroinvertebrates, fish, and macrophytes, along with their trophic interactions. This analysis extends that of Glibert (2010) with a more comprehensive examination of the changes in trophic components and their interactions. Part III considers the complexities of biogeochemical processes and how they relate to changes in the food web. Biogeochemical feedbacks provide the mechanisms whereby food web changes are facilitated when stoichiometry changes. This section examines apparent relationships between the emergence and production of macrophytes, establishment of exotic bivalve molluscs, and blooms of the toxic cyanobacterium *Microcystis aeruginosa*. Part IV compares the Bay Delta to selected freshwater and estuarine ecosystems that have exhibited similar patterns, and Part V compares the ecological stoichiometric and alternate stable state interpretations with some prevailing views of system change in the Bay Delta. Finally, Part VI concludes with a summary of the implications of these ideas with respect to current debates and challenges associated with nutrient management, the development of nutrient criteria, and predictions for system recovery upon nutrient removal. Directions for further study are also suggested.

PART I: EUTROPHICATION, ECOLOGICAL STOICHIOMETRY, NUTRIENT RATIOS, AND ALTERNATE STABLE STATE THEORY

Eutrophication

Although the term "eutrophication" has been variably defined (e.g., Nixon, 1995; Richardson and Jørgensen, 1996; Andersen et al., 2006; Ferriera et al., 2010), central to all definitions is the concept that the enrichment of water by nutrients causes an enhanced biomass and/or growth rate of algae which, in turn, leads to an undesirable disturbance in the balance of organisms present in the water and to the quality of the water body concerned (Burkholder, 2001; Duarte et al., 2008; Glibert et al., 2010; Burkholder and Glibert, 2011). The effects of eutrophication are generally characterized in terms of increased phytoplankton (chlorophyll *a*) in the water column, loss of dissolved oxygen leading to hypoxia or anoxia, loss of submersed aquatic vegetation (SAV), shifts in species dominance across trophic levels, and loss of certain fisheries (Hutchinson, 1973; Cloern, 2001; Schindler, 2006). Increases in many harmful algal species have also been associated with eutrophication (Hallegraeff, 1993; Anderson et al. 2002; Glibert et al., 2005, 2006a, 2010; Glibert and Burkholder, 2006; Heisler et al., 2008).

The ecosystem response to eutrophication is a continual process rather than a static condition or a trophic state (Hutchinson, 1973; Cloern, 2001; Smayda, 2006). Historically, the concept of eutrophication was mostly applied to the natural aging of lakes (Wetzel, 2001); more recently, the terms "accelerated" or "cultural" eutrophication have been used in recognition of major human influences (e.g., Burkholder et al., 2006, 2007). Cloern (2001) suggested three conceptual phases of the understanding of eutrophication and its effects in coastal ecosystems. The first phase considers responses in ecosystems directly related to changes in nutrient loading, including such changes as chlorophyll *a*, primary production, dissolved oxygen, or other measures of system metabolism. The second phase recognizes that estuaries act as filters, modulating the responses, in turn leading to indirect as well as direct effects. Such filters include system typology (e.g., Kurtz et al., 2006; Madden et al., 2010) as well as inherent optical properties. The third phase stresses interactive effects of multiple stressors on a system, including contaminants, exotic or invasive species, aquaculture development, climate change, and hydrological changes, and proposes linkages to synthetic tools to guide management (Figure 2). Here, the suggested conceptual Phase III model of Cloern (2001) is coupled with the ecological stoichiometric framework (Sterner and Elser, 2002) to further understanding not only of the effects of nutrient loading, but also the effects of disproportionate nutrient loading (or nutrient removal).

Ecological Stoichiometry

Ecological stoichiometry provides a framework for "taming" the complexity of both the direct and the indirect responses of ecosystems to eutrophication. Ecological, or elemental, stoichiometry relates the organismal needs for different elements with those of available substrates or, at higher trophic levels, those of available food. Ecological stoichiometry suggests that different organisms will dominate under different relative proportions of critical elements (C, N, or P) due to differences in allocation of C, N, and P in the various structures that form the biomass of different types of organisms (Sterner and Elser, 2002). As noted by Hall (2009, p. 504), "Ecological stoichiometry formalizes what should be obvious: Organisms interacting in food webs are composed of different elements, such as C, N, or P. As a result, energy and nutrient flow through consumer-resource interactions obey fundamental constraints."

Thus, ecological stoichiometry is basically a comparison of nutrient ratios in solution or food and in consumer biomass. An ecological stoichiometric perspective asks the questions: *Do organisms have an elemental balance reflective of their food or their available substrates? If not, why not, and what are the*

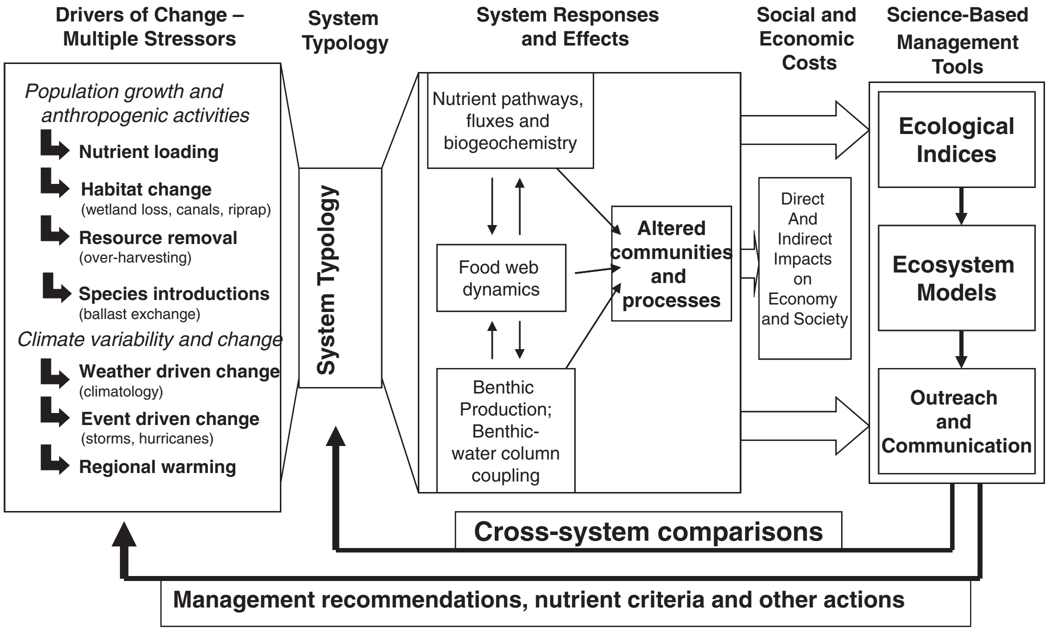

Figure 2 Modified conceptual diagram of the "phase III" model of eutrophication (Cloern, 2001) showing the complexity of interactions and effects of multiple stressors and eutrophication.

ecological consequences? The Redfield ratio (Redfield, 1934, 1958), in which organismal C:N:P ratios are assumed to be in the proportion of 106:16:1 by atoms, is likely the most well-known stoichiometric relationship. Redfield's (1934) work indicated that the N:P ratio of phytoplankton should be approximately 16:1 on a molar basis, and hence, deviations from this ratio (in both the particulate and the dissolved nutrient pools) have been interpreted as evidence of limitation. The Redfield ratio was developed from observations in oligotrophic, pelagic marine waters, where both phytoplankton biomass and nutrient concentrations are low and there is minimal interference from suspended sediments. Changes in this ratio have been compared to shifts in phytoplankton composition, yielding insights about the dynamics of nutrient regulation of phytoplankton assemblages (e.g., Tilman, 1977; Smayda, 1990; Hodgkiss and Ho, 1997; Hodgkiss, 2001; Heil et al., 2007).

Elemental differences in biomass are found at all levels of organismal structure across trophic levels, from the subcellular to the macrocellular structural components (Sterner and Elser, 2002). At the subcellular level, organelles vary in their N:P content. In particular, ribosomes are high in P relative to N; they are "the most P rich and lowest N:P organelles in cells" (Sterner and Elser, 2002, p. 73). Ribosomes are required for growth, and an increase in ribosomes is required for a cell to have an increase in growth rate. This concept has been well illustrated for phytoplankton (Geider and LaRoche, 2002; Sterner and Elser, 2002; Quigg et al., 2003; Finkel et al., 2010). Fast-growing cells have a lower N:P ratio than their more slowly growing counterparts. They have proportionately more allocation of resources to "assembly machinery" (rRNA; high P) than to "acquisition machinery" (protein; high N) (Elser et al., 2003; Klausmeier et al., 2004). In contrast, phytoplankton species that can sustain their metabolism when resources are low—i.e., more slowly growing cells—have a higher proportion of pigments and proteins with proportionately higher N:P ratio (Sterner and Elser, 2002; Elser et al., 2000, Elser, 2006; Arrigo, 2005; Finkel et al., 2010; Figure 3). Slowly growing cells are also generally, but not always, larger in size (e.g., Malone, 1981; Kagami and Urabe, 2001; Finkel et al., 2010). However, slowly growing, nutrient-stressed phytoplankton may also be capable of short-term "luxury" uptake of the limiting nutrient in excess of growth, leading to highly variable N:P ratios under transient conditions (Flynn, 2002); thus, the change in N:P ratio with algal growth rate is not necessarily a linear function (Ågren, 2004).

The question of whether N:P ratios or individual nutrients regulate phytoplankton growth has long been debated (e.g., Tilman and Kilham, 1976; Tilman, 1977; Bulgakov and Levich, 1999; Reynolds, 1999). Reynolds (1999, p. 29) pointedly asked the question, "When both [N and P] are 'not limiting', . . . how is it possible for the ratio of growth-saturating resources to influence the growth?" He then answered this question by stating (p. 31), ". . .there should be no selective effect, consequential upon different affinities of storage capabilities for a nutrient resource, that might distinguish between the potential performances of any pair of planktonic algae, so long as the resource concentrations are able to saturate the growth demand. If that is true, then the ratio between the (saturating) concentration of any of the resources also fails to exert any regulatory significance." This statement, which summarizes the prevailing view that nutrients are non-regulating in the Bay Delta because they are typically above levels that saturate growth demand, is based on the notion that growth rate (i.e., productivity) is the only process by which nutrients impact the ecosystem. Ecological stoichiometric theory, on the other hand, recognizes that phytoplankton nutrient composition is sensitive to available nutrients even when supplied in excess, and that the nutritional composition of the phytoplankton can play an important role in selecting and structuring the upper trophic level organisms. The emphasis is on the transfer of elements (N and P, as well as C and other elements) through the food web rather than the rate of production of organic C.

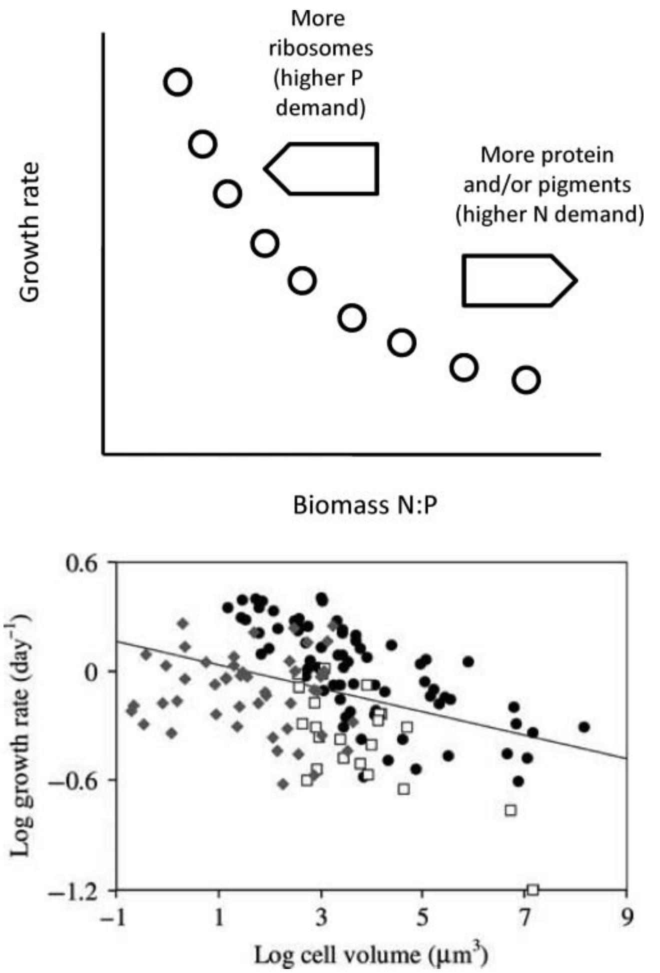

Figure 3 (A) Generalized relationships between the intrinsic growth rate of organisms and the N:P ratio in the biomass of those organisms. (B) Size dependence (cell volume, μm^3) of temperature-corrected growth rate (day^{-1}) for a range of phytoplankton functional groups: diatoms (◆), dinoflagellates (☐), and other taxonomic groups (●) (a combination of cyanobacteria, chlorophyte, haptophyte, cryptophytes, and various other groups). Line indicates the least-squares regression of all data (log $\mu = -0.06$ log V + 0.1; $R^2 = 0.15$). This figure is reproduced from Finkel et al. (2010), Oxford University Press, with permission. The data were compiled by T. A. V. Rees.

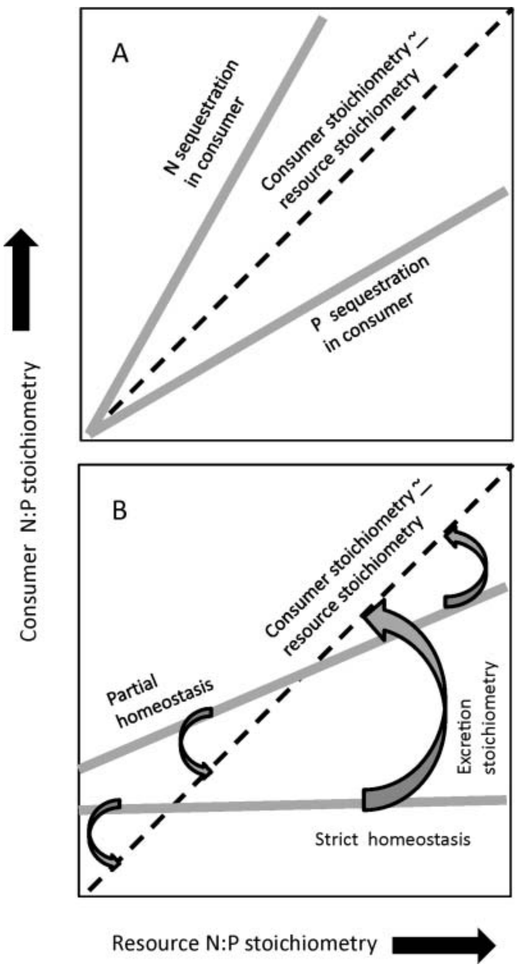

Figure 4 Schematic relationships between resource N:P (either dissolved nutrients or prey) and consumer N:P. The dashed line in both panels represents the hypothetical situation in which the consumer N:P matches that of its resource. (A) Hypothetical situations in which the consumer is either N- or P-enriched relative to its resource in a constant proportion. (B) Hypothetical situations where the consumer either partially or strictly regulates its biomass N:P regardless of the N:P of its resource. The arrows depict the extent to which the excreted or released nutrients differ in N:P from that of the consumer biomass N:P. Excretion N:P is expected to be negatively related to substrate N:P when the consumer N:P is constrained.

Although the Redfield ratio is often used to infer elemental composition in phytoplankton, the actual elemental composition of microalgae in culture and phytoplankton in nature is highly variable (Geider and LaRoche, 2002; Finkel et al., 2010). Due to the ability of many phytoplankton to take up nutrients in excess of their growth demands (e.g., Glibert and Goldman, 1981; Terry et al., 1985), they often follow the "you are what you eat" model (Sterner and Elser, 2002, p. 16), within reasonable limits (Figure 4A). This has been elegantly demonstrated for many phytoplankton in culture. For example, it has been shown that the medium N:P ratio and the cellular N:P ratio of the chlorophyte *Scenedesmus* are very similar when grown over a range of N:P ratios in culture (e.g., Rhee, 1978). Extreme cellular N:P ratios are observed in cultured cells that have experienced limitation of either N or P (Rhee, 1978; Goldman et al., 1979; Geider and LaRoche, 2002) reflecting a non-homeostatic "luxury consumption" response that is characteristic of microalgae (Goldman and Glibert, 1983). Significantly, under nutrient-replete growth conditions (i.e., saturating ambient concentrations), variation in the N:P ratio of microalgae can be on the order of three- to four-fold (5–19 mol N:mol P; Geider and LaRoche, 2002; Finkel et al., 2010). While it may be difficult in field data to differentiate the extent to which this variation is related to changing algal species (or taxonomic groups), culture experiments have clearly demonstrated plasticity in the N:P ratio as a function of growth condition (e.g., Quigg et al., 2003; Leonardos and Geider, 2004a,b; Finkel et al., 2010). In field comparisons, N and P stoichiometry in dissolved substrates have compared favorably with that of particulate matter in some regions (e.g., Glibert et al., 2006b), but a range of relationships between dissolved and particulate matter can be observed.The salient point is that microalgae are not homeostatic with respect to cellular N and P. Moreover, many phytoplankton species or species groups have specific adaptations to life under "non-Redfieldian" conditions (Glibert and Burkholder, 2011).

Thus, while Reynolds (1999) and others have convincingly explained how individual nutrients, not ratios, regulate the *growth* of phytoplankton, their interpretation does not address how the wide plasticity of cell quotas (sensu Droop, 1973) in algae under nutrient-saturated conditions alters the elemental *quality* of the algal food available to grazers. In other words, while primary production can constrain secondary production, N and P availability to the phytoplankton can regulate the types of organisms found in the upper trophic levels via effects of elemental composition at the primary producer level (Figure 4).

Compared to algae and other primary producers, heterotrophs are relatively inflexible in their stoichiometry (McIntyre and Flecker, 2010). As emphasized by Sterner and Elser (2002, p. 254), "as one ascends the pelagic food web . . . trophic groups grow increasingly nutrient and especially P rich. . .," because there is a greater need for P in skeleton and bone than in skin, heart, kidney, muscle, or brain. The latter tissues and organs all have a relatively high N content (Sterner and Elser, 2002). In aquatic food webs, small fish that have a higher muscle:skeleton ratio than large fish thus tend to have a higher biomass N:P ratio. Omnivorous fish, such as the Centrarchidae, are generally larger than planktivorous fish, have more bone and skeleton, and have particulary high P content (Sterner and Elser, 2002). Whereas whole-fish N content generally varies across a relatively small range (∼8–11%), whole-fish P content tends to vary five-fold, from ∼1–5% (Sterner and George, 2000; Figure 5).

In addition to the varying elemental requirements of their macromolecular structures, grazers are able to stabilize their biomass stoichiometry more than phototrophs, because they have more excretion and release pathways to eliminate the nutrients that that are not needed. By excreting, egesting, or respiring what they do not need, an effective feedback develops with respect to the element stoichiometry of their resource or prey (Figure 4B). A difference between food resource N:P ratios and consumer N:P ratios becomes established, and when consumers

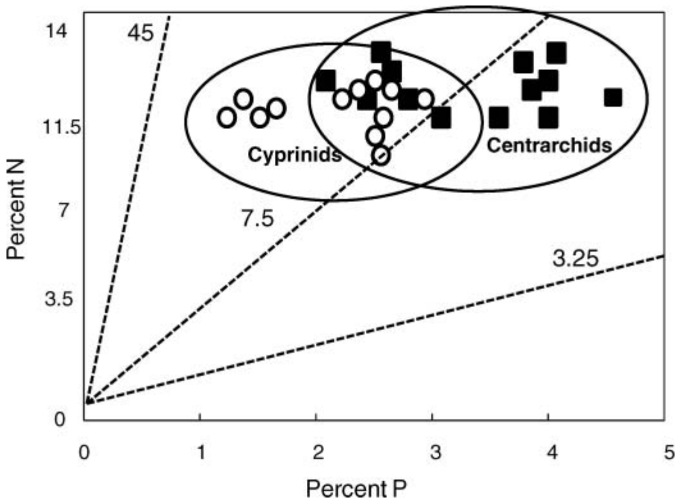

Figure 5 Relative N and P content of cyprinid and centrarchid fish. The dashed lines give three N:P ratios for perspective. Figure is modified and redrawn from Sterner and George (2000).

ingest nutrient-poor food, their need to dissipate those nutrients ingested in excess increases (Vanni et al., 2002). Ultimately, species of grazers that can sequester the nutrient in least supply relative to their needs, while dissipating what they do not need, should become the dominant (and, in some cases, the keystone) species by outcompeting grazers that cannot effectively acquire what they need and/or dissipate what they do not. As noted by Sterner and George (2000, p. 127), "Nutrient flux from resources to consumers and then to waste products can be thought of as a chemical reaction wherein *mass must balance*" (emphasis added). Moreover, as noted by Malzahn et al. (2007, p. 2063) based on Brett (1993), "stoichiometric needs of secondary consumers and the stoichiometry of prey are normally finely tuned." This means that fish, with their relatively inflexible skeletal requirements, have a greater likelihood to be limited by nutrients than by energy or other factors (McIntyre and Flecker, 2010). Larger organisms are greater sinks of nutrients than smaller organisms, and thus, their impacts on nutrients are evident over longer temporal and spatial scales.

Fish excretion varies in the proportion by which materials are egested (feces, pseudofeces) and excreted (urine production), as well as by the species and their osmotic environment, with NH_4^+ excretion typically being more episodic and concentrated in saltwater environments and more dilute and continuous in freshwater environments (e.g., Randall and Wright, 1987). Schindler and Eby (1997) showed that obligate planktivores are most likely to recycle nutrients at high N:P ratios. McIntyre and Flecker (2010, p. 553), in a broad survey, found that "the N:P ratio of excreted nutrients increased substantially with body size; on average, large fishes excreted relatively more N than P compared to smaller counterparts." Large fish also play a proportionately larger role in nutrient translocation, especially from benthic to pelagic environments (Vanni, 1996, 2002).

Ecological stoichiometry principles would predict that the dominant predator, if its biomass N:P ratio is tightly constrained, should have a biomass N:P ratio that is inversely related to the N:P ratio of the ambient nutrient pool, and homeostasis from nutrient recycling will drive the nutrient balance of the system to be self-sustaining (Figure 4B). Such principles further suggest that biodiversity should be a consequence of stoichiometry, and that populations should self-stabilize as a result of stoichiometric constraints. As summarized by Sterner and Elser (2002, p. 263), the balance of multiple chemical elements has many consequences for community dynamics: "Stoichiometry can either constrain trophic cascades by diminishing the chances of success of key species, or be a critical aspect of spectacular trophic cascades with large shifts in primary producer species and major shifts in ecosystem nutrient cycling."

Yet, homeostasis comes at a cost, typically as a reduction in the rates of growth or reproduction (Boersma, 2000; Boersma and Kreutzer, 2002; Boersma et al., 2008). The relative balance of nutrients affects all aspects of behavior (i.e., in meeting nutritional demands), growth rate, fecundity, and ultimately, the success of different populations (Jeyasingh and Weider, 2005, 2007). Stoichiometry also affects various life stages differently (Moe et al., 2005, p. 31): "[a]n organism's requirements for different elements may vary throughout its life cycle, and thus certain life stages may be more sensitive than others to variation in the stoichiometry of its resource." As a specific example, there is a greater need for C, N, and P for developing copepod juveniles, but at a later stage, while C is still needed for metabolism, more P must be allocated to eggs; thus, P-poor food can disproportionately affect egg production while not affecting survival (Færøvig and Hessen, 2003; Laspoumaderes et al., 2010).

It must be noted, however, that stoichiometric regulation of trophic interactions can be modulated when "good food goes bad" (sensu Mitra and Flynn, 2009). Many attributes of food can be altered chemically and physiologically, leading to trophic interactions that would not be anticipated strictly on the basis of elemental stoichiometry. As examples, production of allelopathic compounds or toxins, or even physical aggregation of cells, can alter trophic transfer.

Alternate Stable State Theory

The alternate stable state theory was developed to describe the general state of shallow, productive lakes (Scheffer et al., 1993, 2003). This theory states that a system will develop a stable state condition; i.e., homeostasis will prevail until an environmental change or disturbance occurs. This change alters the positive reinforcing feedbacks of homeostasis, and the system is shifted to a new stable state: hysteresis overcomes homeostasis (Scheffer et al., 1993; Scheffer and Carpenter, 2003). Such shifts can be abrupt (e.g., Tátrai et al., 2009). Communities may not return to their original state when the disturbance is removed. Recent interest in stable state theory has occurred because of efforts to restore macrophyte dominance in systems that have become dominated by phytoplankton as a consequence of increased eutrophication (e.g., Bachmann et al., 1999; Poor, 2010). Thus, the intersection of eutrophication, ecological stoichiometry, and stable state theories addresses the question: *To what extent is ecosystem structure altered when nutrient loads are altered?*

Both direct and indirect interactions among organisms help to stabilize assemblages (Vanni, 2002). Trophic cascades and food chain interactions result from predator–prey interactions, the release of organisms from predation pressure, propagated effects on both the biotic and abiotic environment, and changes in availability of substrates, among many other factors. Nutrient loading ("bottom-up" control) and grazing ("top-down") control are ultimately interconnected at several levels. First, selective grazing alters nutrient regeneration. This has been well demonstrated at the microbial level. For example, macrozooplankton, such as copepods, can both enhance and reduce the flow of regenerated N. On the one hand, they release N directly, but how much and in which form depends on what they ate and how long ago they ate it (Bidigare, 1983; Miller and Glibert, 1998). Macrozooplankton also graze on both phytoplankton and microzooplankton, which are consumers and regenerators, respectively, of N (Caron and Goldman, 1990; Glibert, 1998). Copepods further stimulate NH_4^+ regeneration by bacteria through the release of organic substrates during feeding and metabolism (Roman et al., 1988; Glibert, 1998) and by preying on larger microzooplankton that relieve smaller microzooplankton from predation, in turn resulting in higher NH_4^+ regeneration (Glibert et al., 1992; Miller and Glibert, 1998; Glibert, 1998). Similar interactions occur from size-selective predation by benthic invertebrates or fish (Vanni, 2002). Food web stability or balance thus depends on interactions at all levels, and factors that alter the balance of nutrients also alter the balance of animal-mediated recycling, leading to new relationships that can affect multiple trophic levels (Vanni, 2002).

A second means by which bottom-up and top-down controls are interconnected relates to the coupling of the benthic and pelagic communities. When external nutrient loads (bottom-up control) are altered, top-down control is affected by the shift in nutrient dynamics from the water column to the sediment where nutrient reserves are accessed by those organisms capable of doing so. These organisms, in turn, alter the habitat for grazers. Exemplified by shallow lakes, the typical stable states are pelagic-phytoplankton-dominated systems and littoral-macrophyte-dominated systems (Scheffer et al., 2003; Peckham et al., 2006; Mieczan, 2010). Blindow et al. (1993) found that systems dominated by macrophytes, such as hydrilla (*Hydrilla verticillata*), are in a unique stable state. Shifts from one state to another have been described as a function of turbidity and light availability (Scheffer et al., 1993), nutrient loading (McClelland and Valiela, 1998; Meiczan, 2010), toxic ammonia levels (Van der Heide et al., 2010), and changes in macrophyte abundance due to mechanical harvesting (Scheffer et al., 2003), as well as other effects.

Regime shifts represent another way to conceptualize alternate stable states. Regime shifts due to climate change and stochastic events, such as storms, are well recognized in ecological and biogeochemical sciences. Regime shifts also involve shifts in food webs (e.g., Ives and Carpenter, 2007) through habitat alteration or species introductions into new areas. Such regime shifts in species are considered difficult to predict and model, but clues about regime shifts are provided in the variance of biomass or chemical constituents of aquatic ecosystems (Carpenter and Brock, 2006). Regime shifts have often been illustrated by marble-in-cup diagrams (e.g., Scheffer et al., 1993, 2001; Amemiya et al., 2007). The likelihood of an ecosystem (marble) being moved to a new state (new cup) is a function of system resilience. When the dynamic structure of the ecosystems is changed, restoration of the original stable state is much more difficult, if possible. Overall, "disentangling . . . effects of anthropogenic stressors in human-altered systems and the potential for other stressors to exacerbate these effects" (Breitburg, 2002, p. 775) requires a comprehensive, multi-dimensional view linking nutrients to physiological responses, trophodynamics and food web structure, and biogeochemistry.

Summary of Part I

System responses to nutrient loading (eutrophication), changes in the relative composition of the nutrient pools (ecological stoichiometry), and the extent to which hysteresis overcomes homeostasis (altered stable states) are all interwoven concepts in nutrient-altered aquatic ecosystems. Trophodynamic interactions are consequences of elemental stoichiometry, physiological adaptation of autotrophs and heterotrophs, and biogeochemical nutrient feedback processes. Food web structure as a whole is highly stoichiometrically constrained. These principles are illustrated below for the Bay Delta food web.

PART II: LONG-TERM TRENDS AND ECOLOGICAL STOICHIOMETRY RELATIONSHIPS WITH THE FOOD WEB OF THE SAN FRANCISCO ESTUARY

This section begins with a description of the sources of data that were analyzed, the data analysis approach and terminology, along with an overview of the long-term trends in freshwater flow, nutrients, and community structure of the Bay Delta. Then, ecological principles of stoichiometry relevant to each major trophic level are described, relating the available Bay Delta data to those principles. Following Smith (2006), this analysis is based on annualized data. Annual nutrient means have been shown to be highly related to chlorophyll *a* over broad data sets worldwide (Smith, 2006; Boynton and Kemp, 2008).

The stoichiometry of N and P is emphasized, as these two important macronutrients have undergone the largest changes over the past several decades. Silicate ($Si(OH)_4$) is not considered here because temporal changes in $Si(OH)_4$ have been smaller than those of N and P over the past several decades. A

Table 1 Sources of data used in this analysis and the time periods over which data were averaged. Stations identified and not shown in Figure 1 can be found on the web sites indicated

Parameter	Units	Data transformation	Temporal period averaged	Spatial area averaged	Source/reference
Water quality					
Ambient nutrients	mg-N L^{-1}, mg-P L^{-1}, or μM	Log-transformed	Average of all values March–November	EMP stations D4, D6, D7, and D8	http://bdat.ca.gov/
Conductivity	μmhos/cm	Normal	No averaging	EMP station D24 at Rio Vista	http://bdat.ca.gov/
pH		Normal	Average of all values March–November	EMP Stations D4, D6, D7, and D8	http://bdat.ca.gov/
Effluent nutrient loads	mg-N L^{-1} or μM	Normal	Monthly or annual	Point source discharge	Central Valley Regional Water Quality Control Board
Phytoplankton					
Total chlorophyll *a*	μg L^{-1}	Log-transformed	Average of all values March–November	EMP stations D4, D6, D7, and D8	http://bdat.ca.gov/
Species composition	Cells mL^{-1}	Log-transformed	Average of all values March–November	EMP stations D4, D6, D7, and D8	http://www.nceas.ucsb.edu/
Zooplankton					
Species composition	no. m^{-3}	Log-transformed	Average of all values March–November	Stations NZ028, NZO32, NZ042, NZ048, NZO54, NZO60, and NZD06	http://www.nceas.ucsb.edu/
Invertebrates					
Mysid shrimp	no. m^{-3}	Log-transformed	Average of all values March–November	Stations NZ028, NZO32, NZ042, NZ048, NZO54, NZO60, and NZD06	http://www.nceas.ucsb.edu/
Total crabs	no. m^{-2}	Log-transformed	Average of all values of *Cancer magister* and *Eriocheir sinensis*, March–November	Bay Study stations 427–736, 837	http://www.nceas.ucsb.edu/
Clams	count/grab	Log-transformed	Average of all values of *Corbula amurensis*, March–November	EMP stations D4, D6, D7, and D8	http://bdat.ca.gov/
Fish					
FMWT catch per tow		Log-transformed	September–December	Stations 401–707 and 801–804	http://www.nceas.ucsb.edu/
FMWT index		Log-transformed	Index covers September–December trawls		http://www.dfg.ca.gov/delta/projects.asp?ProjectID=FMWT
STN index		Log-transformed	Index covers June–July trawls		http://www.dfg.ca.gov/delta/projects.asp?ProjectID=TOWNET
FMWT fish length	mm	Catch weighted average (reject years with counts <6)	September–December	Stations 401–707 and 801–804	http://bdat.ca.gov/
Beach seine	Relative abundance	Log-transformed	September–December		http://bdat.ca.gov
Other abiotic parameters					
X2	km	Normal	Average of all values March–November	Distance of salinity = 2 isohaline from Golden Gate Bridge	http://www.water.ca.gov/dayflow/

comprehensive analysis of this nutrient and its relationship to N and P merits separate analysis.

Data Sources

Publically available databases (mostly 1975–2005) were used for all analyses of the Bay Delta (Table 1). This system has an extensive monitoring program in place that covers a wide range of parameters, including physical variables, water chemistry, phytoplankton, zooplankton, invertebrates, and fish. Flow data were obtained from the California Department of Water Resources day flow record (http://www.water.ca.gov/dayflow/). All nutrient, chlorophyll *a*, and phytoplankton data were obtained from the Interagency Ecology Program Bay Delta and Tributary project data portal (accessed from http://www.bdat.ca.gov/, now available at http://www.water.ca.

gov/iep/products/data.cfm). Wastewater effluent data were obtained from the Central Valley California Regional Water Quality Control Board (2010; http://www.waterboards.ca.gov/ centralvalley/). Phytoplankton data, available as densities of individual taxa counts, were grouped into abundant functional groups: Bacillariophyceae (diatoms), Chlorophyceae (green algae), Cryptophyceae (cryptophytes), Dinophyceae (dinoflagellates), and Cyanophyceae (cyanobacteria). Individual species identifications are only considered for selected potentially harmful species. Cyanobacteria are underestimated in these long-term data because the recent expansion of *Microcystis* (Lehman et al., 2005, 2008, 2010; Baxa et al., 2010) is not well represented in the taxa counts. Picocyanobacteria are not included because they are not routinely enumerated. Zooplankton data were retrieved from the monthly zooplankton surveys conducted by the California Department of Fish and Game (http://www.dfg.ca.gov/delta/); these data do not include microzooplankton. Data on abundance of the invasive clam, *Corbula amurensis* (formerly *Potamocorbula amurensis*) were also obtained from the Interagency Ecological Program database (http://bdat.ca.gov/, now available at http://www.water.ca.gov/iep/products/data.cfm). Fish data were provided by the California Department of Fish and Game (http://www.dfg.ca.gov/delta/). Many of these data have been compiled by the National Center for Ecological Synthesis (NCEAS Project 12192, Ecosystem analysis of pelagic organism declines in the Upper San Francisco Estuary; http://www.nceas.ucsb.edu/projects/12192), and these compilations have been used where available. Because of the wide range of organisms considered here, species are generally referred to by their genus names or their common names rather than their species names.

The geographic coverage of the chemical, microbial, and macroinvertebrate data extends from the confluence of the Sacramento and San Joaquin Rivers to Suisun Bay, inclusive. However, the fish indices, such as the fall midwater trawl (FMWT) Index, may have included catches from higher in the Sacramento River, the central and southern Delta, and/or the San Joaquin River above its confluence with the Sacramento River.

All data from other comparative systems were obtained from literature sources or from the authors' measurements, described below.

Data Analysis

Data from the primary growing season (spring to fall) were averaged for most parameters (Table 1) and compared annually. All nutrient and abundance data were first tested for normality and, if found to be skewed, were log-transformed. Nutrient ratios were not transformed because they were normally distributed. Bivariate scatterplots were developed between organismal abundance and individual nutrients (total P [TP], phosphate [PO_4^{3-}], and NH_4^+ or nutrient ratios [dissolved inorganic N:TP {DIN:TP} and DIN:dissolved inorganic P {DIN:DIP}]), and Pearson correlations and/or coefficients of determination were calculated.

Pairwise relationships between biological parameters and nutrients and/or nutrient ratios were determined using both the original data and data that were adjusted for autocorrelation. The Durbin-Watson test was used to test for autocorrelation (Durbin and Watson, 1950, 1951). While only some variables displayed autocorrelation (Durbin Watson D $\sim$2), all relationships among the data were explored using several approaches. Data were analyzed as (1) original data (log-transformed if appropriate), (2) stationarized by trend (pre-whitened), (3) stationarized by first-difference, and (4) smoothed using a three-year backward moving average. The reason for applying several approaches is that different approaches for removing autocorrelation may lead to different types of errors (e.g., Pyper and Peterman, 1998). While failure to remove autocorrelation may lead to Type I errors (increased chance of concluding a correlation is significant when it is not; Jenkins and Watts, 1968), removing autocorrelation may lead to the opposite—Type II errors (failing to reject a null hypothesis of no correlation when a correlation exists; Pyper and Peterman, 1998). This comparison was also motivated by the concern summarized by Pyper and Peterman (1998, pp. 2134 and 2136) in their analysis of covariates and fish, "removing autocorrelation (low-frequency variability) may limit a researcher's ability to detect the common effect of some slowly changing variable on fish population dynamics. . . . By removing time trends, we are assuming that they are unrelated, yet there are obvious mechanisms that could produce common time trends among recruitment data such as trends in environmental variables, habitat degradation, or trends in the abundance of competitor, prey, or predator species (e.g., Butler, 1991)." By comparing all approaches here, the relative importance of directional versus cyclic (or other higher frequency) variability could be assessed. When correlations are lower for pre-whitened or first-differenced data compared to the original or smoothed data, the analysis suggests that low-frequency, slowly changing components of variability (i.e., directional changes) are dominant, whereas when pre-whitened or first-differenced correlations are greater, higher-frequency components of variability likely are greater (Pyper and Peterman, 1998). Significance was assessed at the $p < 0.05$ and 0.01 levels; n was adjusted by parameter and test to account for parameters with missing data and to account for autocorrelation in the smoothed data.

Nutrient Ratios and Terminology

Although N:P ratios can be useful in a relative sense, the same ratio can be obtained from markedly different numerators and denominators, as long as their proportions remain the same. Thus, an elevated N:P ratio, suggestive of P limitation, can be obtained by a depletion in P (true P limitation), or by an increase in N without a corresponding depletion in (non-limiting) P. The latter is the case, for example, for the mouth of the Mississippi River, USA, where elevated N:P ratios have resulted from excess loading of N rather than from decreasing P (Justic et al., 1995; Rabalais et al., 1996; Turner and Rabalais, 2004; Dodds, 2006). Nutrient ratios are applied here to illustrate the potential stoichiometric regulation of the food web (i.e., through food quality and biogeochemistry influences) rather than to infer the potential for nutrient limitation of phytoplankton assemblages.

Most applications of N:P ratios consider only inorganic forms of N and P. Different ratios may be obtained depending upon the form(s) specifically included in the ratio (Dodds, 2003, 2009). The perspective of N or P limitation or availability may be different depending upon whether the N:P ratio is calculated solely with inorganic forms of N and P, or with both inorganic and organic forms, or with the particulate fraction only, or with just the dissolved fractions. For example, on the western Florida shelf, the mean N:P ratio of the water off the Caloosahatchee River in May of 2003 was considerably less than Redfield proportions when only inorganic forms of N and P were considered, leading to a conclusion of an N-limited system, but when the ratio of organic nutrients were included, the proportions suggested a P-limited system (Heil et al., 2007). Karl et al. (2001) reported similar findings for the Hawaii time series station. Determining whether to include the organic fractions of N and P (DON and DOP) in such ratios may depend upon the degree to which the organic fractions are bioavailable to the specific organisms present. Unfortunately, much still is not known about the bioavailability of most organic N and P constituents (Seitzinger et al., 2002b; Berman and Bronk, 2003). While nearly all algal species can use all forms of inorganic N and P, their use of organic nutrients is much more variable. The calculation of nutrient ratios also changes depending upon whether chemical interactions with particulate matter are taken into consideration. Nutrients, especially P, interact with particulate matter (via both adsorption and desorption), and the interactions can result in deviations in both particulate and dissolved N:P ratios. Dissolved inorganic PO_4^{3-} (=DIP) is equivalent to soluble reactive phosphate, SRP, but is referred to as PO_4^{3-} or DIP throughout.

Thus, because different nutrient ratios may give different perspectives on nutrient relationships, both DIN:TP and DIN:DIP were used here. In accordance with recommendations by Dodds (2009), DIN:TP can serve as a "reliable surrogate" for total N:TP (TN:TP), understanding that such a substitute may underestimate the true TN:TP.

Table 2 Abbreviations and acronyms used throughout the text

DIN	Dissolved inorganic nitrogen
DIP	Dissolved inorganic phosphorus; used here interchangeably with phosphate, PO_4^{3-}; equivalent to soluble reactive phosphorus
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphorus
FMWT	Fall midwater trawl fish index
POD	Pelagic organism decline; the rapid decline in numerous planktivorous fish species in the Bay Delta since 1999
SAV	Submersed aquatic vegetation
SRP	Soluble reactive phosphorus
SRWWTP	Sacramento Regional Wastewater Treatment Plant
STN	Summer townet fish index
TN	Total nitrogen
TP	Total phosphorus
WWTP	Wastewater treatment plant
X2	In the Bay Delta, the distance from the Golden Gate Bridge at which salinity is measured to be 2

The most frequently used abbreviations and acronyms used throughout this review are summarized in Table 2.

Long-Term Trend Overview

The long-term trends in freshwater flow, nutrient loading, and biota in the Bay Delta have been previously described (e.g., Kimmerer et al., 2000; Kimmerer, 2002, 2004; Bennett, 2005; Jassby, 2008; Glibert, 2010). Here, a brief review is provided for context, focusing on trends associated with the region between the confluence of the Sacramento and San Joaquin Rivers to Suisun Bay. Each nutrient and component of the food web is described in more detail in subsequent sections.

The early to mid-1980s represented a period of relatively high flow, whereas the late 1980s represented a period of lower flow, and the early 1990s had very low flow (Figure 6). Flow

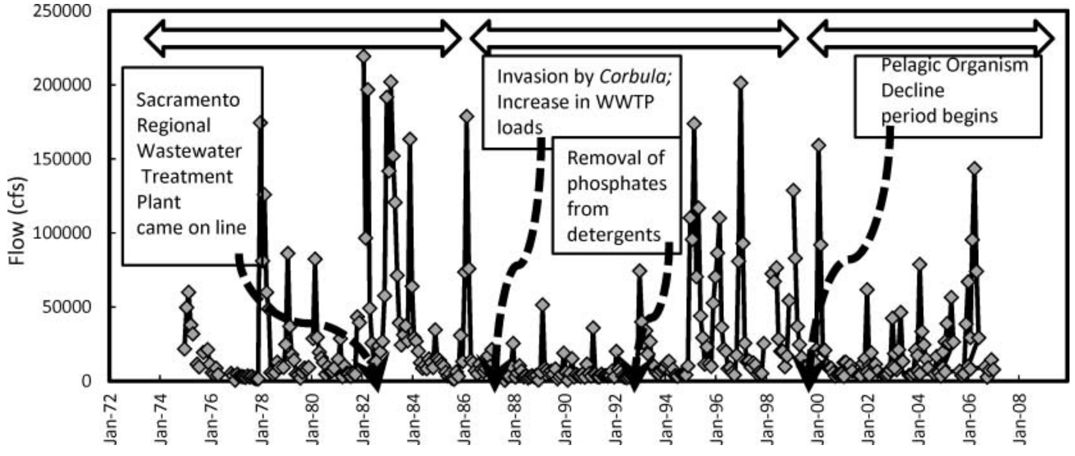

Figure 6 Time course of the change in freshwater outflow from the Bay Delta over time and notations indicating the time of major changes in nutrients and the food web. The arrows along the top of the graph depict the major time periods that are described in text. The first time period is from the start of the time series up to the time when the WWTP discharge began. The second time period encompassed the period of major change in N and P. The third time period corresponds to the "POD." The text boxes and dashed arrows highlight key events.

Table 3 Average nutrient concentration (mg L^{-1}), nutrient ratio (wt:wt), and chlorophyll *a* (μg L^{-1}) for time periods shown and overall percent change in the parameter from the first to third time period

Time period	Ammonium	Nitrate + nitrite	DIP	TP	DIN:TP	DIN:DIP	Chlorophyll *a*
1975–1986	3.70	17.40	2.19	4.71	4.48	9.63	9.03
1987–1999	4.47	25.79	2.83	4.79	6.31	10.70	2.16
2000–2005	5.36	25.62	2.29	3.81	8.12	13.53	2.40
Percent change	44.9	47.2	4.5	−19.1	81.25	40.5	−73.4

increased in the late 1990s and decreased in the early 2000s, but this latter period of low flow was not as low as in the early 1990s.

Phytoplankton biomass (as chlorophyll *a*) was high in the 1970s, often reaching values > 30 μg L^{-1}, but declined sharply in the mid-1980s following invasion of the exotic clam, *Corbula amurensis* (Alpine and Cloern, 1992; Kimmerer et al., 1994; Kimmerer, 2004; Jassby, 2008). Diatom relative abundance also declined in the early 1980s, and dinoflagellates, cryptophytes, and chlorophytes were generally the dominant phytoplankton groups in the late 1980s to mid-1990s (Brown, 2010). Cyanobacteria, including *Microcystis*, increased beginning in the late 1990s through the early 2000s (Lehman et al., 2005, 2008, 2010).

Dominant copepod species also changed over time. Calanoid copepods *Eurytemora affinis* and *Acartia clausii* were dominant in the 1970s and early 1980s. The calanoid copepod *Sinocalanus doerrii* first appeared in the late 1970s (Orsi et al., 1983). The calanoid copepod *Pseudodiaptomis forbesi,* also an exotic species, began increasing a decade later, followed by the invasive cyclopoid copepod *Limnoithona tetraspina* (Orsi and Walter, 1991; Kimmerer, 2004). In the fresher reaches of the Bay Delta and in years of higher flow, *Daphnia magna* has also been an important member of the zooplankton community (Müller-Solger et al., 2002). The invasive clam *Corbula amurensis* first appeared in significant numbers in Suisun Bay in 1987 (Alpine and Cloern, 1992; Kimmerer et al., 1994; Kimmerer, 2004). It thus appeared around the same time that the copepod *Pseudodiaptomis* increased in abundance.

Pelagic fish populations changed over the past few decades, often coincident with changes in the lower trophic levels. Delta smelt (estimated from both summer townet [STN] or FMWT indices), as well as longfin smelt, began to decline in ∼1982, but their declines accelerated beginning in ∼1999, referred to as the POD period. In contrast, other fish species increased in numbers over the time series, especially largemouth bass (*Micropterus salmoides*) and sunfish (*Lepomis* spp.). Additional changes included increases in invasive macrophytes, especially water hyacinth (*Eichhornia crassipes*) and Brazilian waterweed (*Egeria densa*).

Nutrients

In contrast to conditions in the 1960s and early 1970s when hypoxia was more frequently noted (Nichols et al., 1986), there presently are no such widespread "classic" symptoms of eutrophication (e.g., Cole and Cloern, 1984; Kimmerer, 2004). Eutrophication has been thought to have been reduced due to major changes in sewage discharge (diversions and forms of nutrients discharged) since the 1970s (Jassby, 2008). However, localized hypoxia has been reported, as well as increased frequency of cyanobacterial blooms, especially *Microcystis aeruginosa*, within the past decade (Lehman et al., 2005, 2008, 2010).

Both loadings and concentrations of N and P have changed significantly over time. The extent and timing of these changes differ not only between N and P, but also between forms of N. Average DIN concentrations (Figure 7) were relatively invariant for the first years of this time series (1975–1982), but they increased significantly after 1982, coincident with the increase in loading of N, especially NH_4^+, from the Sacramento Regional Wastewater Treatment Plant (SRWWTP), which came on line at that time, consolidating numerous smaller facilities that were

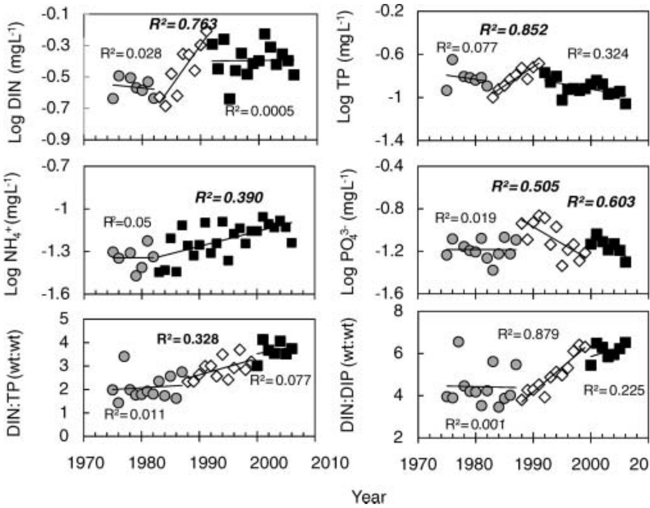

Figure 7 Changes over time in the major inorganic nutrients and inorganic nutrient ratios (log-transformed data) in the confluence of the Sacremento and San Joaquin Rivers to Suisun Bay from 1975–2005. Note that different nutrients changed in different periods of the time course, and thus, the delineation of the time periods by symbols differs from those of subsequent graphs; these individual time periods highlight the periods of major change. For panels showing total inorganic N (DIN) and TP, the time course highlights 1975–1982 (●), 1983–1992 (◇), and post-1992 (■). For PO_4^{3-}, DIN:TP, and DIN:DIP, the time course highlights the periods of 1975–1986 (●), 1987–1999 (◇), and post-1999 (■). For NH_4^+, the time course highlights the period of 1975–1982 (●) and post-1982 (■). Coefficients of determination (R^2) of all time periods are shown; those indicated in bold are significant at $p < 0.05$, those in bold italic are significant at $p < 0.01$. Note that in addition to the trends in time periods indicated, the overall trends in NH_4^+ ($R^2 = 0.21$, $p < 0.05$), DIN:TP ($R^2 = 0.65$, $p < 0.01$), and DIN:DIP ($R^2 = 0.46$, $p < 0.01$) were significant.

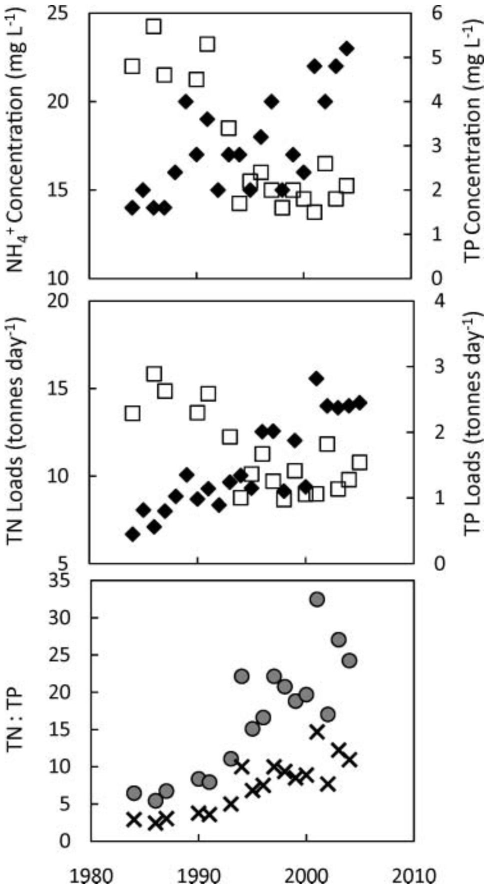

Figure 8 Change in concentrations and total loads (NH$_4^+$ or TN, ◆ TP, ☐) and DIN:TP (molar basis, ● weight basis, X) over time in the wastewater effluent of the SRWWTP, located on the Sacramento River.

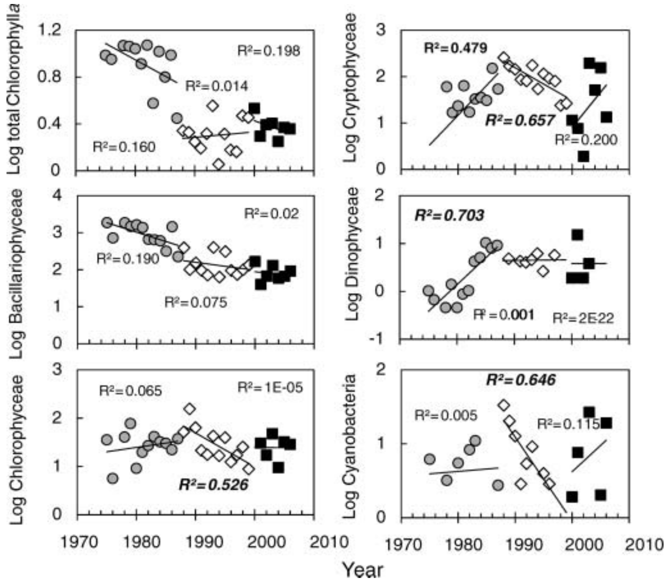

Figure 9 Change in the concentration of chlorophyll *a* (log μg L^{-1}) and abundances of the major classes of eukaryotic phytoplankton and prokaryotic cyanobacteria (log cells mL^{-1}) over the time course. Coefficients of determination (R^2) are given for each major time period (1975–1986, ●; 1987–1999, ◇; and post-1999, ■). Those coefficients indicated in bold are significant at $p < 0.05$, and those in bold italics are significant at $p < 0.01$. The analysis indicates a significant change in abundance over one or more major time periods for diatoms (Bacillariophyceae), green algae (Chlorophyceae), cryptophytes (Cryptophyceae), dinoflagellates (Dinophyceae), and cyanobacteria. In addition, the declines in chlorophyll *a* and diatoms over the entire time course were significant ($R^2 = 0.57$ and 0.68, $p < 0.01$), as was the increase in dinoflagellates ($R^2 = 0.30$, $p < 0.05$).

located upriver (Figures 7 and 8 and Table 3). Both concentrations of effluent discharge and total loads have increased over time; present-day loads of NH$_4^+$ are 12 tonnes day^{-1} (14 tonnes TN), corresponding to concentrations in excess of 25 mg L^{-1} (~1,800 μM-N; Figure 8).

Concentrations of TP, PO$_4^{3-}$, and DIN tracked each other for the period of 1982–~1991, but after that, P concentrations declined, returning to levels approximating those of pre-1982 (Figure 7, Table 3). This decline has been related to the removal of P from laundry detergents (Glibert, 2010), as well as the loss of canneries in the region that had used P in their processing (Van Nieuwenhuyse, 2007). As a consequence of the increased N loads but decreased P loads (Figure 8), DIN:TP and DIN:DIP increased over time (Figures 7 and 8).

Phytoplankton

The relative dominance of different phytoplankton groups has changed over time (Figure 9). Total chlorophyll *a* declined abruptly after 1986 (Figure 9). Diatoms dominated from the start of the time series (1975) to ~1986, although they were already in decline by the mid-1980s when dinoflagellates and cryptophytes were increasing (Glibert, 2010; Brown, 2010). From 1986–1999, diatoms, chlorophytes, cryptophytes, and cyanobacteria declined significantly, but dinoflagellate abundance was relatively stable (Figure 9). After 1999, there was no significant increase in the abundances of crytophytes and cyanobacteria (Figure 9; but note the above-described underestimation of cyanobacteria).

The overall changes in total chlorophyll *a* or the abundance of any algal group relative to concentrations of TP or PO$_4^{3-}$ were not significant when compared as log-transformed data, but there were significant negative correlations in chlorophyll *a*, diatoms (Bacillariophyceae), and green algae (Chlorophyceae) and increases in cryptophytes and dinoflagellates with TP and/or PO$_4^{3-}$ when the data were detrended (Figure 10, Table 4). Declines in chlorophyll *a,* diatoms, and cyanobacteria were significantly correlated with the increase in NH$_4^+$ concentrations in both the original and detrended data (Figure 11, Table 4). When the changes in phytoplankton are considered with respect to nutrient ratios, not only were the declines in chlorophyll *a* and diatoms negatively correlated with DIN:TP and DIN:DIP ratios in the original and detrended data, but also the increase in dinoflagellates was positively correlated with DIN:TP ratios (Figure 12, Table 5). These changes in phytoplankton abundance are generally consistent with expectations from ecological stoichiometric principles. Diatoms tend to have a lower biomass

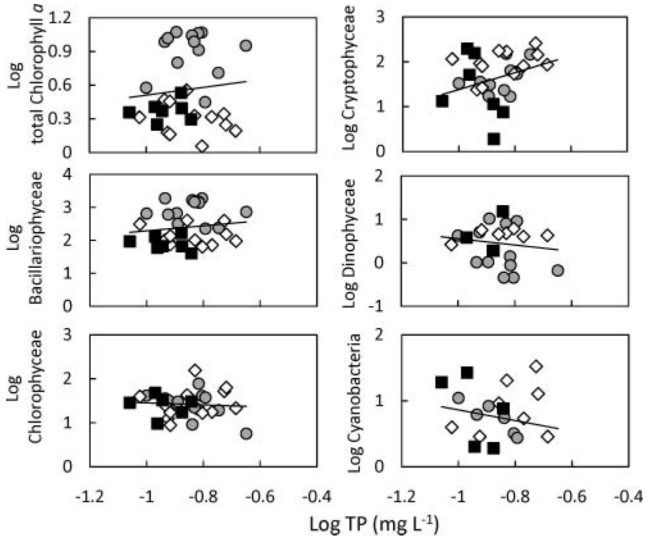

Figure 10 Change in the concentration of chlorophyll *a* (μg L^{-1}) and abundances of the major classes of phytoplankton (log cells mL^{-1}) over the time course in relation to TP (mg L^{-1}) (all data were log-transformed). The major periods are represented by different symbols (1975–1986, ●; 1987–1999, ◇; and post-1999, ■). While these correlations were not significant ($p > 0.05$), several significant relationships emerged when the data were detrended (see Table 4).

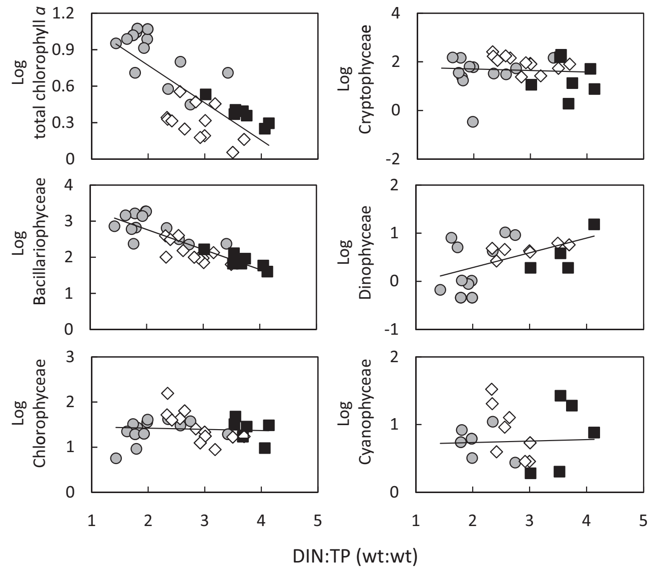

Figure 12 As for Figure 10, except in relation to DIN:TP (wt:wt) (abundance data were log-transformed). The correlations for total chlorophyll *a*, diatoms (Bacillariophyceae), and dinoflagellates (Dinophyceae) indicated significant relationships ($p < 0.05$). Note that chlorophyll *a* and diatoms (Bacillariophyceae) also showed significant correlations with DIN:DIP ($p < 0.05$; see Table 4).

N:P ratio than dinoflagellates, especially harmful dinoflagellates species (Finkel et al., 2010). Low biomass N:P ratios should lead to higher growth rates, due to the high proportion of P required in ribosomes and biomass (Sterner and Elser, 2002; Figure 3), and diatoms generally have higher growth rates than dinoflagellates (e.g. Harris 1986, and references therein).

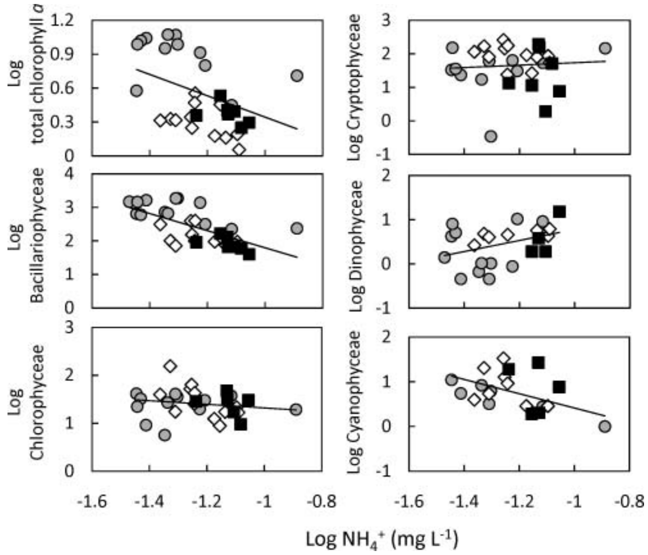

Figure 11 As for Figure 10, except in relation to NH_4^+ (mg L^{-1}) (all data were log-transformed). The correlations for total chlorophyll *a*, diatoms (Bacillariophyceae), and cyanobacteria were significant for these and/or the detrended data ($p < 0.05$; see Table 4).

Zooplankton

Although not included here due to lack of long-term data, the importance of microzooplankton in the San Francisco food web is recognized. The trophic link between phytoplankton and microzooplankton has been demonstrated and may represent an important mediator of C flow and nutrients to the mesozooplankton (Rollwagen-Bollens et al., 2006, 2011).

The composition of macrozooplankton has changed over time in the Bay Delta (Figure 13). The calanoid copepods *Eurytemora*, *Sinocalanus*, *Acartia*, and harpacticoid copepods decreased from roughly the start of the time series to the early to mid-1990s, although the decline in *Acartia* mostly occurred in the mid-to-late 1990s (Figure 13). The decline in these species, especially *Eurytemora*, has been interpreted to be a consequence of increased grazing after the invasive clam *Corbula* became established (e.g., Alpine and Cloern, 1992; Kimmerer, 2004). The invasive calanoid copepod *Pseudodiaptomus* had relatively invariant abundances for its first decade in the estuary and then declined, but it appears to be increasing again. Abundance of the cyclopoid copepod *Limnoithona tetraspina* increased significantly during the mid-1990s, whereas earlier in the time series a different species of *Limnoithona*, *L. sinensis*, was present (Bouley and Kimmerer, 2006). Overall, the ratio of *Eurytemora affinis*/cyclopoid copepods showed a decline in the first part of the time series, and then a relatively stable ratio of abundances (Figure 13).

Over time, the abundances of cladocerans *Bosmina longirostris* and *Daphnia* sp. were similar to that of *Limnoithona* spp., lower in the mid-1980s then rising significantly until the late 1990s (Figure 13). The mysid macrozooplankter *Neomysis*

Table 4 Correlation coefficients (*r*) for the organisms and nutrients shown

	TP (mgL^{-1})				PO_4^{3-} (mgL^{-1})				NH_4^+ (mgL^{-1})			
Organism	Original data	Pre-whitened	First-differenced	Three-year moving average	Original data	Pre-whitened	First-differenced	Three-year moving average	Original data	Pre-whitened	First-differenced	Three-year moving average
Phytoplankton												
Chlorophyll *a* ($\mu g\ L^{-1}$)		−0.44*			−0.33	−0.57**			−0.43*	−0.34	−0.45**	−0.37
Bacillariophyceae (cells mL^{-1})		−0.51**				−0.62**	−0.39*		−0.57**	−0.60**	−0.60**	−0.54**
Chlorophyceae (cells mL^{-1})			−0.44**				−0.43**	−0.413*				0.36
Cryptophyceae (cells mL^{-1})		0.36						0.40*				
Dinophyceae (cells mL^{-1})							0.48**		0.35			
Cyanobacteria (cells mL^{-1})									−0.54*	−0.59*		0.40
Zooplankton												
Eurytemora (individ. m^{-3})		−0.58**			−0.38*	−0.72**		−0.34	−0.37*		−0.56**	−0.40*
Sinocalanus (individ. m^{-3})	−0.43*			−0.43*	−0.66**			−0.65**	−0.49**		−0.61**	
Acartia (individ. m^{-3})	0.56**	0.41*		0.58**	0.39*	0.44*	0.37*			0.45*	0.70**	
Pseudodiaptomus (individ. m^{-3})		−0.45	−0.75**	−0.46		−0.50*	−0.83**		−0.72*	−0.65**	−0.66**	−0.85*
Harpacticoids (individ. m^{-3})				0.48*								−0.48*
Limnoithona (individ. m^{-3})	−0.70**	−0.70**		−0.76**	−0.41*	−0.64**		−0.47*	0.46*			0.54**
Daphnia (individ. m^{-3})	−0.50**	−0.75**	−0.51**	0.54**	−0.71**	−0.72**	−0.75	−0.75**	−0.44*	−0.38*	−0.44*	
Bosmina (individ. m^{-3})	−0.70**	−0.83**	−0.32	−0.74**	−0.85**	−0.85**	−0.34	−0.86**	−0.57**	−0.59**		−0.43*
Neomysis (individ. m^{-3})	0.39*			0.53**			0.46**		−0.49**	−0.53	−0.63*	−0.68**
Invertebrates												
Corbula (count/grab)		0.50*	0.38			0.48*	0.47*		0.64**	0.55*	0.60*	0.84**
All crabs (individ. m^{-2})		0.42*							0.53**	0.42*		0.49*
Crangon (individ. m^{-3})									−0.57**	−0.42*	−0.33	−0.59**
Palaemon (individ. m^{-3})	0.41*								−0.44*			−0.64**
Fish												
Delta smelt (STN index)	0.60**	0.51*	0.45*	0.42							−0.35*	
Delta smelt (FMWT index)				0.52**			−0.50**					
Longfin smelt (FMWT index)		−0.62**			−0.72**	−0.80**		−0.68**	−0.64**	−0.57*		−0.52**
Splittail (FMWT index)				−0.35	−0.51**	−0.49*		−0.68**	−0.34			−0.37
Threadfin shad (FMWT index)			−0.33*	−0.53**								
Striped bass (FMWT index)				0.32					−0.58**			−0.81**
Yellowfin goby (FMWT catch per tow)				0.32			−0.58**		−0.47**	−0.42*	−0.48*	−0.36
Starry flounder (FMWT catch per tow)		0.45*			−0.39*	−0.42*		−0.47*				
Crappie (relative abundance)	−0.65**	−0.69**	−0.39	−0.63**	−0.69**	−0.68**	−0.41	−0.81**				
Sunfish (relative abundance)	−0.69**	−0.58**		−0.83**	−0.46*	−0.65**		−0.53**				0.40*
Largemouth bass (relative abundance)	−0.51**	−0.48**	−0.41*	−0.81**		−0.54**	−0.49**	−0.46**			−0.40*	0.35
Silversides (relative abundance)						0.37*			0.48**	0.44*		0.52**

For each nutrient, the first column shows the correlations of the original data (log-transformed), the second column shows the correlations of the trend stationary data, the third column shows the correlations of the difference stationary data, and the fourth column shows the correlations of the data transformed as three-year backward moving averages. The correlations are for the entire time series. Only values for $p < 0.10$ are shown; values that are significant at $p < 0.05$ are indicated by *, and those significant at $p < 0.01$ are indicated by **. Negative correlations are highlighted in blue and positive correlations are highlighted in pink ($p < 0.05$ [lighter shade] and 0.01 [darker shade] only).

Table 5 Correlation coefficients (r) for the organisms and nutrient ratios shown

	DIN:TP (wt:wt)				DIN:DIP (wt:wt)			
Organism	Original data	Pre-whitened	First-differenced	Three-year moving average	Original data	Pre-whitened	First-differenced	Three-year moving average
Phytoplankton								
Chlorophyll *a* (μg L^{-1})	−0.76**	−0.40*	−0.57**	−0.77**	−0.53**		−0.57**	−0.50**
Bacillariophyceae (cells mL^{-1})	−0.53**	−0.58*	−0.45**	−0.93**	−.63**		−0.45**	−0.72**
Chlorophyceae (cells mL^{-1})								−0.42*
Cryptophyceae (cells mL^{-1})								−0.41*
Dinophyceae (cells mL^{-1})	0.53*		0.48*	0.49*	0.36			
Cyanophyceae (cells mL^{-1})			−0.33					
Zooplankton								
Eurytemora (individual m^{-3})	−0.75**	−0.34	−0.55**	−0.83**	−0.46**		−0.54**	−0.53**
Sinocalanus (individual m^{-3})	−0.42*			−0.34		0.49**		
Acartia (individual m^{-3})	−0.41*		0.40*	−0.60**	−0.45**		0.40*	−0.56**
Pseudodiaptomus (individual m^{-3})	−0.66**	−0.64**		−0.80**				−0.62**
Harpacticoids (individual m^{-3})	−0.69**			−0.90**	−0.66**		−0.39	−0.76**
Limnoithona (individual m^{-3})	0.68**			0.73**	0.81**	0.45*		0.88**
Daphnia (individual m^{-3})		−0.35						
Bosmina (individual m^{-3})		−0.35	0.44				0.44*	
Neomysis (individual m^{-3})	−0.88**	−0.62**	−0.54**	−0.96**	−0.81**	−0.62**	−0.52**	−0.93**
Invertebrates								
Corbula (count/grab)	0.67**	0.51*	0.73**	0.81**	0.45*			0.56*
All crabs (individual m^{-2})	0.53**	0.48*		0.58**				0.54**
Crangon (individual m^{-3})	−0.76**	−0.49**	−0.43*	−0.77**	−0.49**			
Palaemon (individual m^{-3})	−0.74**		−0.40*	−0.93**	−0.57**		−0.47*	−0.76**
Fish								
Delta smelt (STN index)	−0.41*		−0.36*				−0.36*	
Delta smelt (FMWT index)	−0.36*			−0.35				
Longfin smelt (FMWT index)	−0.65**	−0.60**		−0.64**				
Splittail (FMWT index)	−0.36	−0.42*		−0.33		0.38*		
Threadfin shad (FMWT index)			0.64*	0.56**	0.35*	0.35*	0.60**	0.50**
Striped bass (FMWT index)	−0.73**			−0.86**	−0.58**			−0.77**
Yellowfin goby (FMWT catch per tow)	−0.49**	−0.45*	−0.64**	−0.43*				0.34
Starry flounder (FMWT catch per tow)	−0.38*			−0.50**				
Crappie (relative abundance)						0.34		
Sunfish (relative abundance)	0.63**			0.77**	0.73**	0.42*		0.84**
Largemouth bass (relative abundance)	0.46*			0.80**	0.48**	0.39*		0.75**
Silversides (relative abundance)	0.54**		−0.40*	0.74**		−0.39*	−0.40*	0.49**

For each nutrient ratio, the first column shows the correlations of the original data (organism data log-transformed), the second column shows the correlations of the trend stationary data, the third column shows the correlations of the difference stationary data, and the fourth column shows the correlations of the data transformed as three-year backward moving averages. The correlations are for the entire time series. Only values for $p < 0.10$ are shown; values that are significant at $p < 0.05$ are indicated by *, and those significant at $p < 0.01$ are indicated by **. Negative correlations are highlighted in blue, and positive correlations are highlighted in pink ($p < 0.05$ [lighter shade] and 0.01 [darker shade] only).

mercedis was abundant in the early years but declined significantly from the mid-1980s to 1999 (Figure 13; Winder and Jassby, 2010). From 2000 to 2005, *Neomysis* began to increase in abundance once again (Figure 13).

In relation to TP and PO_4^{3-} concentrations, *Limnoithona*, *Daphnia*, and *Bosmina* were negatively correlated in the original data, and *Eurytemora* and *Pseuodiaptomus* were also correlated in the detrended data (Figure 14, Table 4). In contrast, *Acartia* abundance was significantly positively correlated with TP and PO_4^{3-} concentrations (Figure 14, Table 4). For *Daphnia*, this relationship is consistent with recent modeling efforts that show that maximum *Daphnia* growth occurs in the range of ∼20–40 μg L^{-1} TP and declines with increasing TP (Persson et al., 2007; Park and Goldman, 2008).

In relation to NH_4^+, the abundances of *Eurytemora, Sinocalanus*, *Pseudodiaptomis*, harpacticoids, *Daphnia*, *Bosmina*, and *Neomysis* were significantly negatively correlated, while those of *Acartia* (detrended analysis only) and *Limnoithona* were positively correlated (Figure 15, Table 4). Thus, when zooplankton abundances were examined in relation to DIN:TP and DIN:DIP ratios, many of the relationships were highly significant (Figure 16, Table 5). Of particular note are the overall significant declines in *Eurytemora*, *Acartia*, *Pseudodiaptomis*, and *Neomysis* in relation to increasing

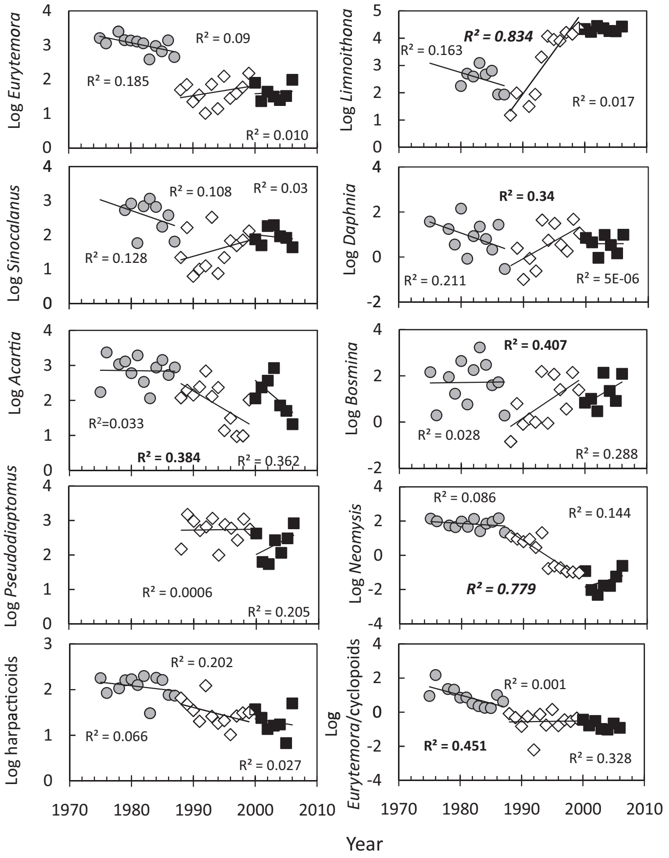

Figure 13 Change in the abundance of the major groups or taxa of zooplankton (as individuals m^{-3} and as the ratio of *Eurytemora affinis*/cyclopoids) over time (all data were log-transformed). Coefficients of determination (R^2) are given for each major time period (1975–1986, ●; 1987–1999, ◇; and post-1999, ■). Those indicated in bold are significant at $p < 0.05$, and those indicated in bold italic are significant at $p < 0.01$. The analysis indicates significant changes over a major time period for most taxa. Among the significant negative relationships over the entire time period (1975–2005) were the declines in *Eurytemora* ($R^2 = 0.65$, $p < 0.01$), *Neomysis* ($R^2 = 0.83$, $p < 0.01$), and the *Eurytemora affinis*/cylopoid ratio ($R^2 = 0.65$, $p < 0.01$).

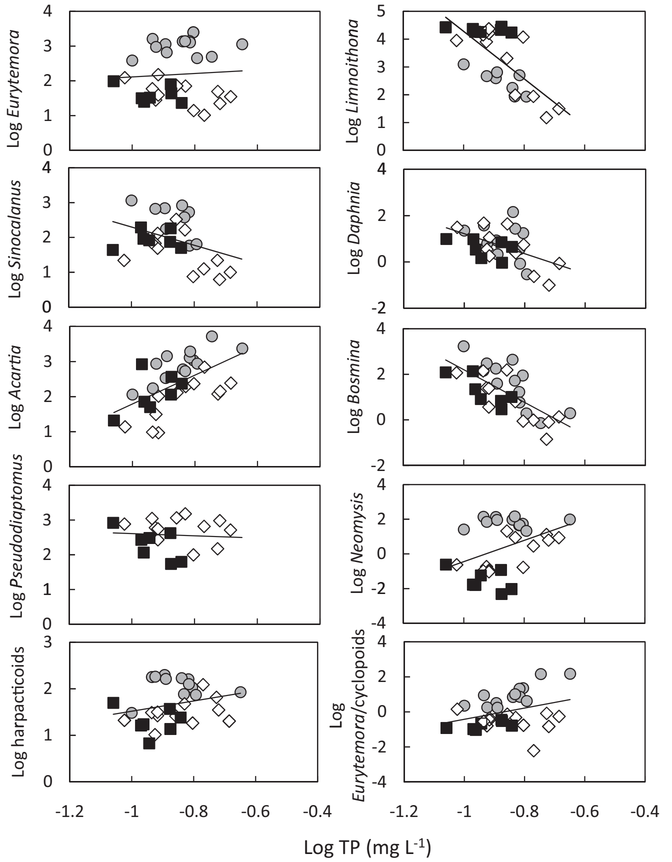

Figure 14 Change in the abundance of the major groups or taxa of zooplankton (as individuals m^{-3} and as the ratio of *Eurytemora*/cyclopoids) over the time course in relation to TP (mg L^{-1}) (all data log-transformed). The major periods are represented by different symbols (1975–1986, ●; 1987–1999, ◇; and post-1999, ■). The correlations for all taxa and groups except the harpacticoids were significant ($p < 0.05$) for these and/or the detrended data (see Table 4).

DIN:TP or DIN:DIP ratios (Figure 16), as well as the increases in *Limnoithona* (Figure 16).

These changes in zooplankton composition are consistent with ecological stoichiometric principles that predict that consumers that successfully sequester the nutrient in least supply relative to their needs should dominate and, in so doing, may stabilize at a new stable state. Calanoid copepods generally have a high N:P ratio of their biomass, ~20–35 by atoms, whereas *Daphnia* and cyclopoid copepods have N:P ratios much closer to Redfield atomic ratios (Walve and Larsson, 1999; Sterner and Elser, 2002). Calanoid copepods thus generally retain N while excreting nutrients in a lower N:P ratio than their biomass (i.e., they release proportionately more P), while cyclopoid copepods and cladocerans have a high P requirement in biomass and, therefore, excrete nutrients in a higher N:P ratio than their biomass (i.e., they release proportionately more N; Hessen, 1997; Sterner and Elser, 2002; Figure 17). In direct measurements under a range of conditions, NH_4^+ excretion measurements of the calanoid copepod *Acartia tonsa* have been very low, consistent with relative retention of N by these animals (Checkley and Miller, 1988; Miller and Glibert, 1998).

Studies from whole-lake experimentation suggest that the N:P ratio is linked to alterations in zooplankton size, composition, and growth rate, as those animals with increased RNA allocation will grow at higher rates due to increased protein synthesis rates (Sterner and Elser, 2002). Similar findings were reported from annual studies in the Baltic Sea (Walve and Larsson, 1999). Hassett et al. (1997) compared the ecological stoichiometric constraints on zooplankton in 31 lakes and 21 marine systems, and their data were strongly suggestive of stoichiometric controls, especially P constraints in the lake systems. In their comparison, the most pronounced nutrient deficiency was found in systems that lacked large piscivores, i.e., those dominated by the planktonic food web. In a laboratory study where *Acartia tonsa* was fed diatoms grown on different N concentrations, Kiørboe (1989) confirmed that this zooplankter changes its feeding rate in response to phytoplankton of different chemical composition—thus, in response to food quality.

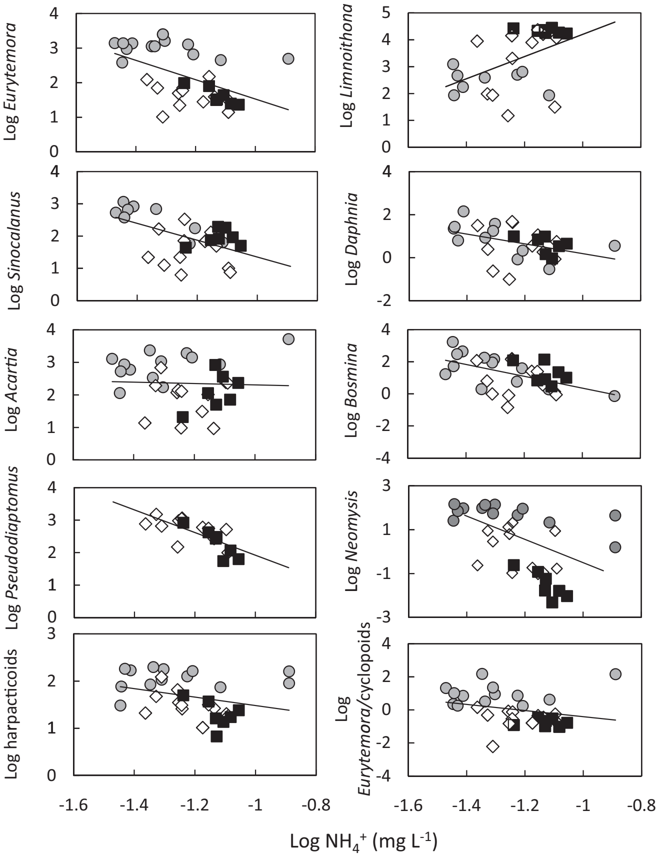

Figure 15 As for Figure 14, except in relation to NH_4^+ (mg L^{-1}) (all data were log-transformed). All correlations for all taxa and groups and for the ratio of *Eurytemora*:cyclopoids were significant ($p < 0.05$) for these and/or the detrended data (see Table 4).

Macroinvertebrates

Major changes in macroinvertebrate composition and abundance have occurred in the Bay Delta over the past several decades. Most significant is the appearance of the invasive clam *Corbula amurensis*. Crabs (including *Cancer magister*–Dungeness and *Eriocheir sinensis*–Chinese mitten) have also changed over time, with significant increases in the years before the mid-1980s, then a period of highly variable abundance, followed by declines post-1999 (Figure 18). Shrimp (*Crangon franciscorum*–crangonid, *Crangon nigricauda*–blacktail, and *Palaemon macrodactylus*–Oriental) either showed no change or modest declines prior to 1999, followed by more substantial declines in recent years (Figure 18). *Corbula* abundances were positively correlated with TP and PO_4^{3-} in the detrended data (Table 4). The abundances of *Corbula* and the crab species were significantly positively correlated with NH_4^+ concentrations, while abundances of the shrimp taxa were negatively correlated with NH_4^+ (Figure 18, Table 4). Consequently, the changes overall in *Corbula* and crabs were positively correlated with DIN:TP ratios, while changes in shrimp were negatively correlated with DIN:TP or DIN:DIP ratios (Figure 18, Table 5).

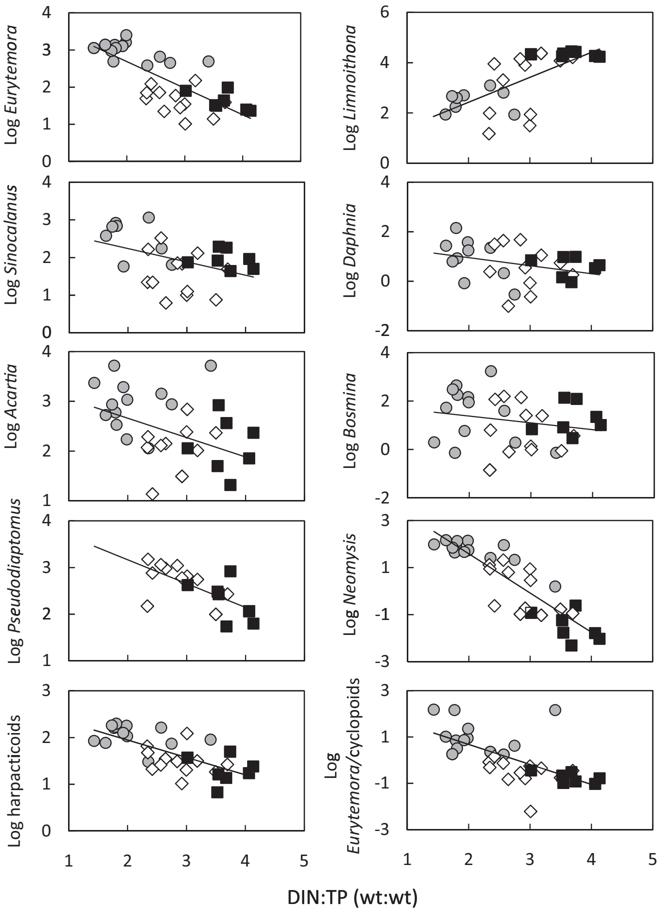

Figure 16 As for Figure 14, except in relation to DIN:TP (wt:wt) (abundance data were log-transformed). All correlations for all taxa and groups were significant ($p < 0.05$) for these and/or the detrended data. Note that the correlations for *Eurytemora*, *Sinocalanus*, *Acartia*, harpacticoids, *Limnoithona*, *Bosmina*, and *Neomysis* with DIN:DIP were also significant ($p < 0.05$) for these and/or the detrended data (see Table 4).

Stoichiometric interpretation of these relationships suggests that *Corbula* may tolerate elevated NH_4^+ levels and may release higher proportions of N than P, whereas shrimp appear to sequester N or are inhibited by elevated NH_4^+ concentrations and may release higher relative proportions of P.

Fish Composition

The changes in fish community composition have also been significant. Many of these changes have previously been attributed to invasive species introductions, some intentional and some accidental. Among those identified as invasive are "largemouth bass, white and black crappie, bluegill, threadfin shad, striped bass, inland silversides, white catfish, black and brown bullhead, and common carp" (Moyle, 2002, p. 31).

As described above, many of the planktivorous fish are in decline (Figure 19). Among these are delta smelt and threadfin shad, which feed on copepods generally in open waters, and longfin smelt, which are more likely to feed on copepods

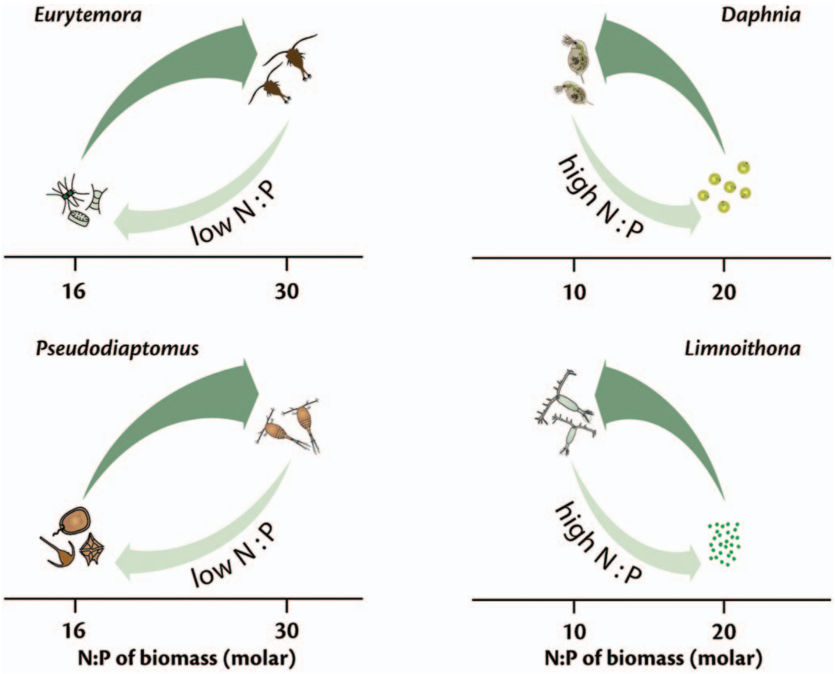

Figure 17 Conceptual diagram of the ecological stoichiometric relationship between different phytoplankton and zooplankton genera. The *x*-axis represents the biomass N:P of the organisms. The wide arrow represents ingestion of the phototrophs by the grazer; the lighter arrow represents nutrient regeneration in the grazer's excretions. Note that the stoichiometry of the regenerated nutrients differs with zooplankton taxon and the N:P ratio of the food on which they graze (color figure available online).

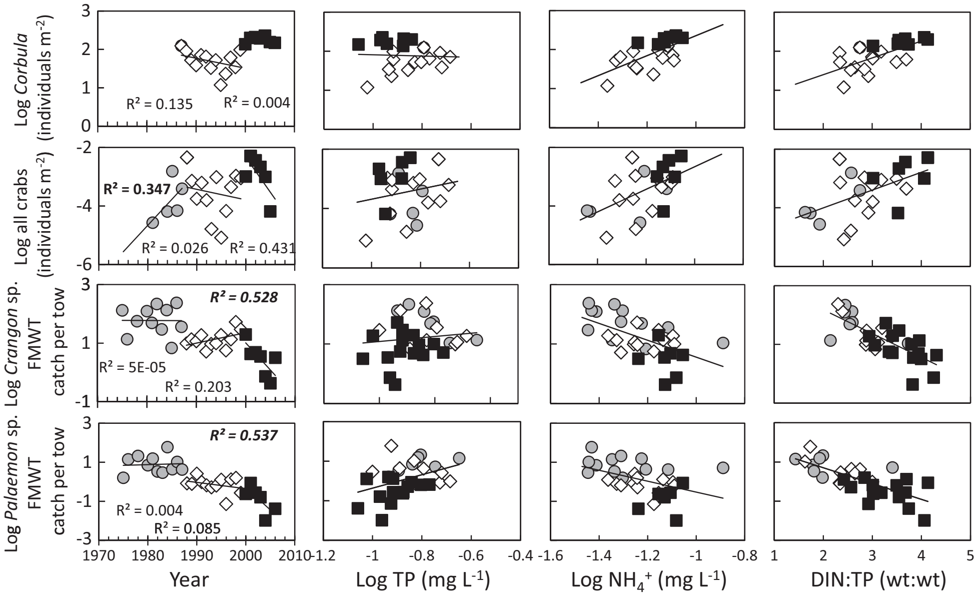

Figure 18 Change in the abundance of *Corbula amurensis* (individuals m^{-2}), crabs (*Cancer magister* and *Eriocheir sinensis,* individuals m^{-2}), shrimp (*Crangon franciscorum*, *Crangon nigricauda,* and *Palaemon macrodactylus*, FMWT catch per tow) over the time course and in relation to TP, NH_4^+, and DIN:TP ratios (all data except DIN:TP log-transformed). Coefficients of determination (R^2) are given for each major time period (1975–1986, ●; 1987–1999, ◇; and post-1999, ■) over the time course. Those indicated in bold are significant at $p < 0.05$, those in bold italics are significant at $p < 0.01$. The analysis indicates a significant change in abundance of the "crabs" grouping over the first major time period and declines in the shrimp species in the third time period. In addition, over the entire time course (1975–2005), the changes in *Crangon* sp. and *Palaemon* sp. were significant ($R^2 = 0.51$ and 0.65, $p < 0.01$, respectively). The relationships between changes in *Corbula*, "all crabs," and *Palaemon* and TP were significant ($p < 0.05$), as were all species and NH_4^+ and DIN:TP for these and/or the detrended data (see Table 4).

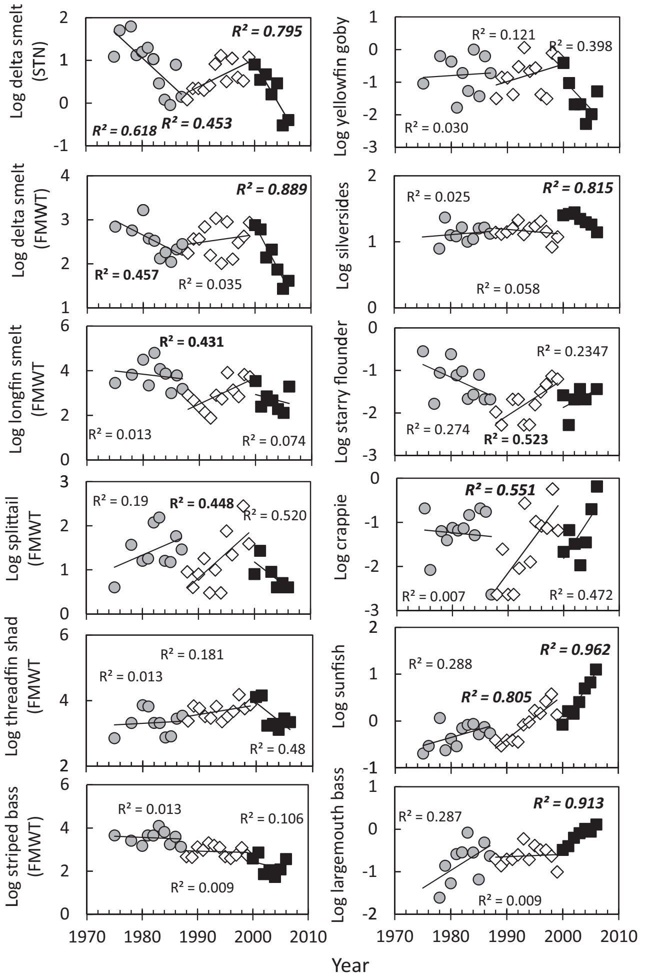

Figure 19 Change in the abundance of major fishes (all data were log-transformed) over the time course. Delta smelt are shown for the STN and FMWT indices. Longfin smelt, splittail, threadfin shad, and striped bass are shown for the FMWT index. Yellowfin goby and starry flounder are FMWT catch per tow. Inland silversides, crappie, sunfish, and largemouth bass are shown as relative abundance based on the beach seine data. Coefficients of determination (R^2) are given for each major time period (1975–1986, ●; 1987–1999, ◇; and post-1999, ■). Those indicated in bold are significant at $p < 0.05$, those in bold italics are significant at $p < 0.01$. The analysis indicates significant changes over one or more major time periods for 9 of the 12 taxa. Although changes were not significant for individual time periods for striped bass, they were significant for the entire time course ($R^2 = 0.671$, $p < 0.01$). Several other species also had significant changes over the entire time course.

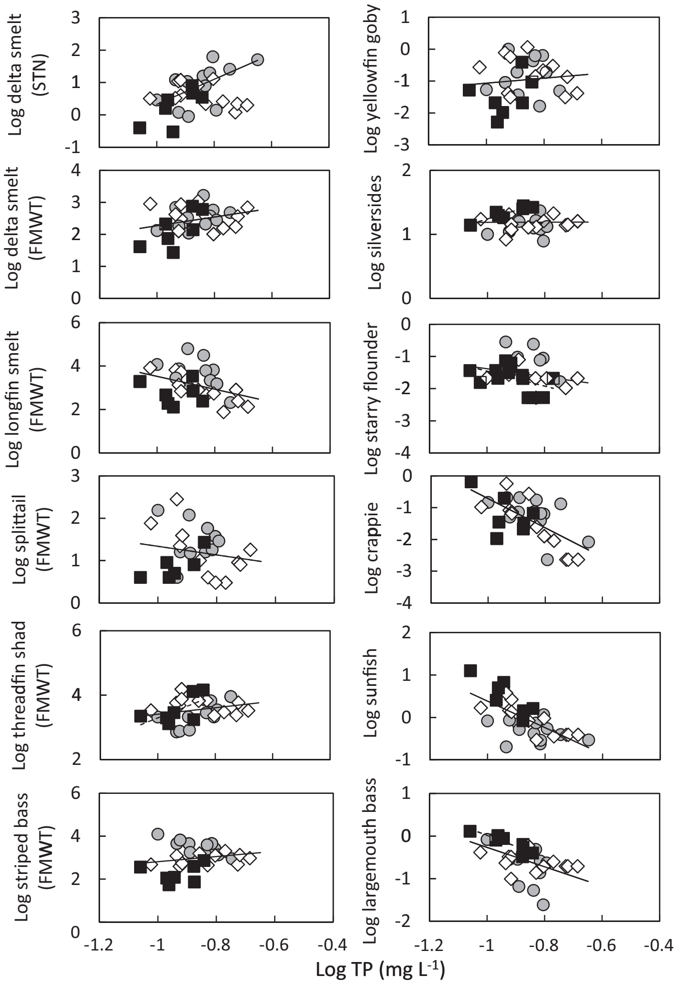

Figure 20 Change in the abundance of major fishes over the time course in relation to TP (mg L^{-1}) (all data were log-transformed). Abundances are as described in Figure 21. The major periods are represented by different symbols (1975–1986, ●; 1987–1999, ◇; and post-1999, ■). The correlations for delta smelt (STN but not FMWT), longfin smelt, crappie, sunfish, and largemouth bass were significant in these data, and for threadfin shad and starry founder in the detrended data ($p < 0.05$; see Table 4).

and opossum shrimp (*Neomysis*) in brackish regions (Moyle, 2002). Inland silversides have similar feeding strategies to smelt (Moyle, 2002). Delta smelt are found from Suisun Bay to the northwest delta and the lower Sacramento River (Moyle, 2002). They preferentially feed on the calanoid copepod *Eurytemora*, although the calanoid copepod *Pseudodiaptomis* has increased in importance in their diet. Increased spring mortality has been linked to the decline in their food availability (Moyle, 2002; Kimmerer, 2004).

Striped bass were introduced in the late 1900s (Moyle, 2002). While successful in the early 20th century, the young of the year (which dominate the FMWT index) have declined since the early 1980s (Figure 19). Prevailing thoughts on the reasons for this decline include, "(1) climatic factors, (2) south Delta pumps, (3) other [water] diversions, (4) pollutants, (5) reduced estuarine productivity, (6) invasions by alien species, and (7) exploitation" (Moyle, 2002, p. 369). Among the many factors thought to be related to the decline in delta smelt is the invasion of silversides, which share much of the same diet and habitat (Bennett and Moyle, 1996).

Among the omnivorous fish in the Bay Delta are striped bass, white catfish (*Ameiurus catus*), channel catfish (*Ictalurus punctatus*), and largemouth bass. Crappie (*Pomoxis* sp.); sunfish and largemouth bass increased significantly in the same years (Figure 19). For many fish, as well, the mid-1980s was also a period of rapid or abrupt change.

Several of the changes in fish abundance were directly and significantly correlated with TP or PO_4^{3-} concentrations (Figure 20, Table 4). Specifically, delta smelt (STN index) was

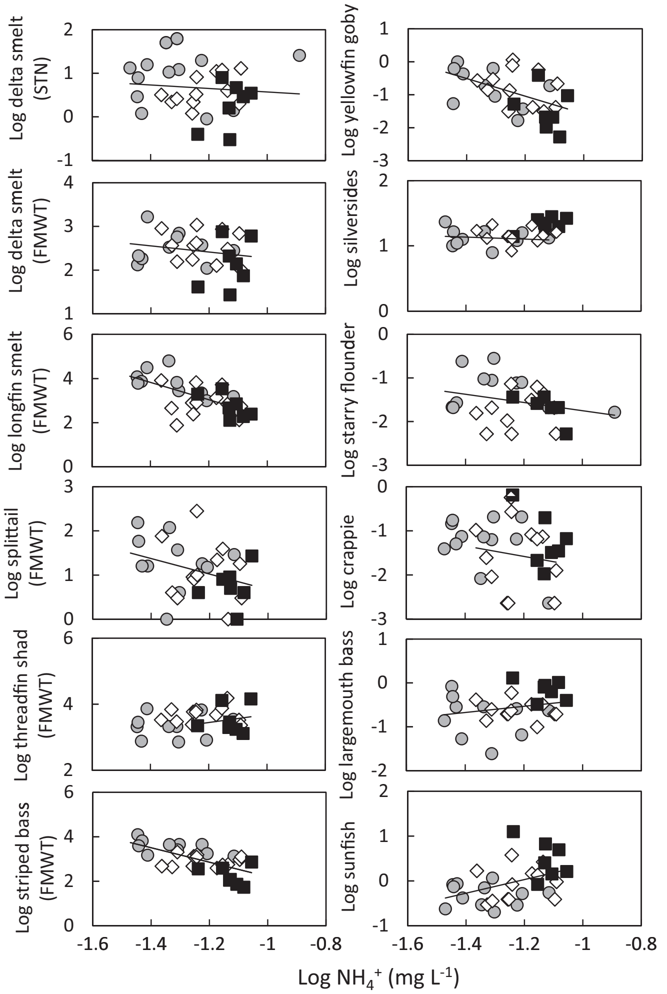

Figure 21 As for Figure 20, except in relation to NH_4^+ (mg L^{-1}) (all data were log-transformed). The correlations for all fish except delta smelt FMWT, splittail, threadfin shad, crappie, and sunfish were significant ($p < 0.05$) in these and/or the detrended data (see Table 4).

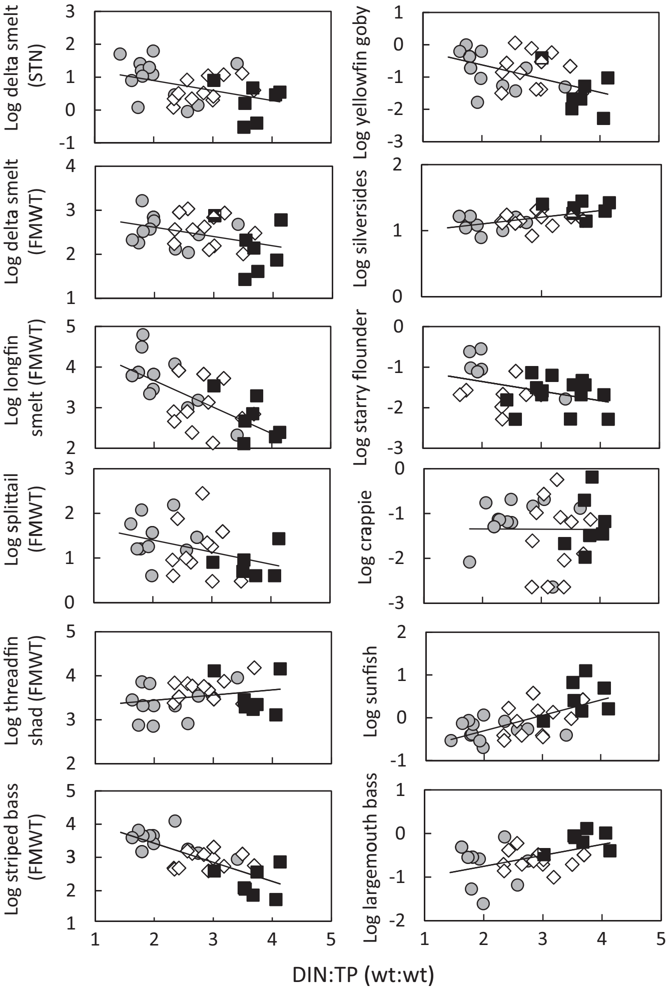

Figure 22 As for Figure 20, except in relation to DIN:TP ratio (wt:wt) (all abundance data were log-transformed). The correlations for all fish except crappie were significant ($p < 0.05$) in these and/or the detrended data. Note that most of these correlations were also significant for DIN:DIP as well (see Table 4).

positively correlated with TP, while abundances of longfin smelt, splittail, starry flounder, crappie, sunfish, and largemouth bass were significantly negatively correlated with TP and/or PO_4^{3-} in the original and detrended data. The abundances of longfin smelt, striped bass, and yellowfin goby were significantly negatively correlated with NH_4^+ concentrations, while those of inland silversides were positively correlated (Figure 21, Table 4). Thus, overall, delta smelt (STN index), longfin smelt, striped bass, and yellowfin goby were negatively correlated with DIN:TP or DIN:DIP ratios, while threadfin shad, sunfish, and largemouth bass were positively correlated with DIN:TP or DIN:DIP ratios (Figure 22, Table 5).

These trends also support the premise that nutrient stoichiometry propagates up the food chain (cf., Malzahn et al., 2007, 2010; Boersma et al., 2008). Ecological stoichiometry theory predicts that systems that shift from low to high N:P ratios should sustain shifts from planktivores to piscivores or omnivores (Sterner and Elser, 2002). The abundances of omnivores or piscivores (crappie, sunfish, largemouth bass) were negatively related to TP concentrations; they have a higher P demand and seemingly can sequester this nutrient more efficiently. The planktivores, with a lower P demand, are apparently less efficient at sequestering P and generally showed either no relationship with P or evidence of a positive relationship with P, especially in the latter years of the time series. Planktivorous fish and calanoid copepods have similar relationships with N:P ratios, whereas omnivorous fish have relationships with N:P ratios that are more similar to those of cyclopoid copepods (Table 5). Sequestration of P in the biomass of the omnivorous fish (with more skeleton and bones) would lead to them being proportionately more abundant when P is less available in the water column.

These findings are consistent with Hendrixson et al. (2007), who showed that the plankivorous fish, less capable of sequestering P, were the most susceptible to P limitation. Hendrixson et al. (2007) also found that bluegills (*Lepomis macrochirus*) only varied in their P content by ∼1% when fish from numerous sites were compared, underscoring strong stoichiometric control. Grazing on P-limited copepods, such as the calanoids or harpacticoids, is considered to enhance P limitation at the level of the planktivores (Boersma et al., 2008). In studies in which nutrients, light, and food chain length were manipulated, the phytoplankton assemblage under low nutrient conditions shifted primarily of cyanobacteria and chlorophytes ("intermediate-" to "poor-quality" food) compared to proportionately more cryptophytes and diatoms under high nutrients ("high-quality" food), and fish body C and P also varied accordingly (Dickman et al., 2008). Vanni et al. (2002) examined the stoichiometry of 28 species of fish and amphibians, and their data suggested that elemental stoichiometric controls were strongest when consumers ingested nutrient-poor items, such as nutrient-limited algae or detritus. The effects were weaker when consumers ingested multiple food items, including other animals that were apparently more nutrient-rich.

The analyses described here have not considered stoichiometric requirements of larvae or seasonal changes. Larvae would be expected to have relatively high P demands due to their high growth rates (Boersma, 2008) and to the shift in resource allocation from muscle growth to bone and fin rays (Malzahn et al. 2007). Boersma et al.'s (2008, p. 484) review specifically noted the potential mismatch between food quality and larval growth: "Larval fish growth typically follows the population increase of herbivorous zooplankton, which succeeds the spring bloom of phytoplankton ... if for some reason the tight coupling of these dynamics becomes less ... it could well be that the larval fish is faced with herbivorous zooplankton that is feeding on late-bloom phytoplankters rather than early bloom ones. Feeding on late-bloom algae automatically implies that the nutrient conditions of these algae are more depleted with respect to P and N and thus these zooplankters are a food source of suboptimal quality for larval fish." Experimentally, nutrient limitation of larval fish has been demonstrated; P-limited tri-trophic food chains had greater effects on fish larval condition than did N-limited food chains (Malzahn et al., 2007). The trajectory of changes in phytoplankton and zooplankton in the Bay Delta over decades as well as with season are consistent with such an effect.

Fish Size

There are many reasons for changes in fish size over time and within individual fish species, and a large variation in body size is frequently observed for a given life history stage (Krebs, 2008). Among the reasons is the availability of adequate nutrition relative to biomass demands. When nutrition is adequate, organisms should grow faster and should reach a larger size. Furthermore, body N:P should decline with animal size due to the higher P demand of larger organisms (Davis and Boyd, 1978). However, there have been variable reports of relationships between fish size and N:P. In a study of bluegills (*Lepomis macrochirus*), higher percentages of P and lower percentages of N were found in larger-sized fish (Davis and Boyd, 1978). On the other hand, Sterner and George (2000) found weak relationships for cyprinids, and Tanner et al. (2000) observed weak relationships for 20 fish taxa in Lake Superior.

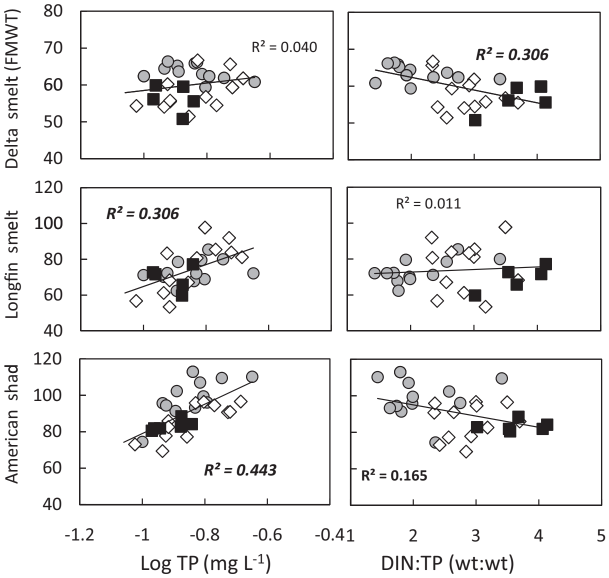

Figure 23 Change in fish length as a function of TP (mg L^{-1}; log-transformed) and DIN:TP (wt:wt). Coefficients of determination (R^2) are given for the entire data set only (symbols as in Figure 19). Those indicated by bold are significant at $p < 0.05$, those by bold italic are significant at $p < 0.01$. The correlations for length versus TP indicate significant relationships for longfin smelt and American shad; the correlations for length versus DIN:TP ratio indicate significant relationships for delta smelt (FMWT) and American shad.

Several fish species of the San Francisco Bay Delta showed strong correlations between their size and either TP concentrations or DIN:TP ratios (Figure 23). Longfin smelt and American shad increased significantly in length with increasing TP, while delta smelt and American shad decreased significantly in relation to DIN:TP ratios (Figure 23). Glibert (2010) previously reported that the size of delta smelt decreased when the zooplankton composition changed from *Eurytemora* dominance to *Pseudodiaptomus* dominance. The data for American shad, an anadromous species, are based on the FMWT surveys, which would capture the early life stages. This would suggest that early feeding is an important determinant of the ultimate size the fish attain.

Trophic Interactions

Comparisons of responses to nutrients across trophic groups provide clues to answering the following questions posed in this analysis, namely: *To what extent do ecosystems self-assemble in a manner consistent with nutrient stoichiometry?* and *Does changing stoichiometry have ecosystem effects even when nutrients are not at levels normally taken to be limiting?* Such relationships were explored here by comparing several key species in relation to other organisms across the nutrient-time gradient.

Diatom abundance varied positively with total chlorophyll *a*, most zooplankton, *Crangon* and *Palaemon* abundance, delta smelt (STN), longfin smelt, and striped bass in the original and the smoothed data (Table 6). In contrast, dinoflagellates, *Limnoithona*, the "all crabs" grouping and sunfish, largemouth bass, and silversides varied negatively with total diatom abundance (Table 6). Most of the same relationships also held when associations with *Eurytemora* were compared (Table 6). It is noteworthy that similar associations between diatoms *Eurytemora* and *Neomysis* and smelt were also observed in the St. Lawrence River estuarine transition zone (Winkler et al., 2003).

Several negative correlations were found between dinoflagellate abundances and higher trophic levels (Table 6). Delta smelt (STN and FMWT) and longfin smelt were negatively correlated with dinoflagellates. Starry flounder (*Platichthys stellatus*) also declined as dinoflagellates increased (Table 6). The dominant dinoflagellate taxon was *Peridinium*, some species of which have been shown to have allelopathic properties that can adversely affect fish (Rengefors and Legrand, 2001, 2007). It is noteworthy that for many algal flagellates, production of bioactive substances increases under P stress (Granéli et al., 1998; John and Flynn, 2002). Most of the correlations between trophic groups were greater for the original and the smoothed data compared to the detrended data. These findings are consistent with the idea that detrending removed a "*common* mechanism influencing [these] data series" (Pyper and Peterman, 1998, pg. 2136). The common mechanism is suggested to be nutrients.

Overall, the Bay Delta food web at the beginning (1975–1986) and end (1999–2005) of the time course shows correspondence with the ratio of the major types of copepods, *Eurytemora affinis*/cyclopoids (Figure 24). These time periods had similar freshwater flow; thus, salinity tolerances should not have been a major factor in food web structuring. When *Eurytemora* were abundant in the early years, the system had higher relative abundances of planktivores (delta smelt, longfin smelt, yellowfin goby). In the later years when cyclopoids became dominant, there was a shift to a more omnivore-dominated community (sunfish, largemouth bass).

Macrophytes

With progressive eutrophication, increased algal production generally occurs at the expense of seagrasses and SAV (Harlin, 1993; Wetzel, 2001; Burkholder et al., 2007 and references therein). Excess N causes native seagrass loss (Burkholder et al., 1992; Short and Burdick, 1996); for example, a nearly complete loss of eelgrass (*Zostera marina* L.) was reported when land-based N loading exceeded 100 kg ha^{-1} yr^{-1} across many systems surveyed (Latimer and Rego, 2010). On the other hand, as nutrient stoichiometry changes, other macrophytes can proliferate (Burkholder et al., 1994, 2007 and references therein).

The macrophyte community of the Bay Delta has changed considerably over the past several decades. Native SAV has largely been replaced by invasive submersed and floating vegetation, including *Egeria densa* and water hyacinth (*Eichhornia crassipes*) (Lund et al., 2007; Santos et al., 2011). Although these changes have disproportionately occurred in the freshwater reaches of the Bay Delta, including the confluence, they potentially have large effects on the entire ecosystem. Water hyacinth apparently was introduced over a century ago (Finlayson, 1983; Gopal, 1987) but has increased in abundance mostly in the past several decades (Finlayson, 1983; Toft et al., 2003). By the early 1980s, water hyacinth covered ~22% of the waterways, in the Bay Delta (Finlayson, 1983). Water hyacinth grows rapidly and has been described to create habitat somewhat similar to the native pennywort (Toft et al., 2003). Although structurally the habitat may be similar, the food web is not. In the Bay Delta, regions heavily overgrown by water hyacinth have been shown to have different epiphytic amphipod species and also a distinctly different fish–invertebrate food web compared to that supported by native pennywort (Toft et al., 2003). Overgrowth of water hyacinth has led to major efforts to control its spread because it blocks waterways. In the late 1990s, chemical control of more than 900 ha of hyacinth in the Bay Delta cost approximately $1,000,000 (California Department of Boating and Waterways [CDBW], 1998; Toft et al., 2003; Anderson, 2003; www.dbw.ca.gov/Environmental/EgeriaDensaGenifo.aspx), but chemical control has been found not to be a cost-effective mitigation strategy (Khanna et al., 2009).

The first appearance of *Egeria* in the Bay Delta is thought to have been in the 1960s, but it increased significantly during the 1980s (Jassby and Cloern, 2000) and even more in the 1990s after a major drought (Anderson, 1999). Although estimated to contribute $\leq$ 10% of the Bay Delta productivity (Jassby and Cloern, 2000), it has been estimated to cover more than ~2,400 ha of area in varying densities (Anderson, 1999, 2003; Hestir et al., 2008, 2010). Of more than 800 sites sampled in 2007 and 2008 in the central delta, *Egeria* was found in > 50% of the samples, about half of which were monospecific patches (Santos et al., 2011). Moreover, in the same study, more than 60% of the waterways were covered with submersed plant canopy, most of which, especially in summer, was *Egeria* (Santos et al., 2011). This species appears to be well adapted to thrive in an altered nutrient and light regime. Under relatively low light, it develops apical shoots more rapidly than under high light, allowing it to reach more light-rich surface waters faster (Rodrigues and Thomaz, 2010).

Table 6 Correlation coefficients (r) for various organisms shown and diatom (Bacillariophyceae), dinoflagellate (Dinophyceae) or *Eurytemora* abundance

	Diatoms (cells mL^{-1})				Dinoflagellates (cells mL^{-1})				Eurytemora (individual m^{-2})			
Organism	Original data	Pre-whitened	First-differenced	Three-year moving average	Original data	Pre-whitened	First-differenced	Three-year moving average	Original data	Pre-whitened	First-differenced	Three-year moving average
Organism												
Phytoplankton												
Chlorophyll *a* ($\mu g\ L^{-1}$)	0.87**	0.70**	0.45*	0.92**	−0.58**			−0.59*	0.93**	0.84**	0.75**	0.96**
Bacillariophyceae (cells mL^{-1})	x	x	x	x	−0.61**			−0.59*	0.89**	0.70**	0.80**	0.95**
Chlorophyceae (cells mL^{-1})								0.61*				
Cryptophyceae (cells mL^{-1})										−0.32		
Dinophyceae (cells mL^{-1})	−0.61**	−0.34		−0.59**	x	x	x	x	−0.52**			−0.55*
Cyanobacteria (cells mL^{-1})								0.46				−0.46
Zooplankton												
Eurytemora (individual m^{-3})	0.89**	0.70**	0.80**	0.95**	−0.52*			−0.55*	x	x	x	x
Sinocalanus (individual m^{-3})	0.55**			0.54*		−0.47*		−0.71**	0.67**			0.43*
Acartia (individual m^{-3})	0.41*		−0.67**	0.71**				−0.48*	0.51**		−0.64**	0.70**
Pseudodiaptomus (individual m^{-3})	0.44			0.61*			−0.45*		0.40			
Harpacticoids (individual m^{-3})	0.69**			0.93**	−0.39			−0.50*	0.74**	0.34		0.89**
Limnoithona (individual m^{-3})	−0.52**		0.37	−0.57*					−0.39	0.47		−0.43
Daphnia (individual m^{-3})	0.46*	0.60**	0.51*	0.47*	−0.36			−0.62*	0.41*	0.48*		0.43
Bosmina (individual m^{-3})	0.40*	0.65**							0.38*	0.61**		0.37
Neomysis (individual m^{-3})	0.81**		0.51**	0.88**		0.46			0.75**		0.56**	0.76**
Invertebrates												
Corbula (count/grab)	−0.42			−0.75**			0.43					
All crabs (individual m^{-2})	−0.50*	−0.41		−0.51*	0.33*		−0.49*				0.59**	
Crangon (individual m^{-3})	0.74**	0.44*	0.52**	0.82**	−0.41			−0.50	0.72**	0.41*	0.59**	0.78**
Palaemon (individual m^{-3})	0.69**			0.90**				−0.47	0.72**		0.40*	0.85**
Fish												
Delta smelt (STN index)	0.46**			0.55*	−0.76**	−0.57**		−0.81**	0.46**		0.60**	0.59*
Delta smelt (FMWT index)	0.37*				−0.45*	−0.45*		−0.67**				
Longfin smelt (FMWT index)	0.67**	0.65**		0.70**	−0.54**			−0.45*	0.70**	0.68**		0.75**
Splittail (FMWT index)	0.32*								0.40*	0.37*		0.52*
Threadfin shad (FMWT index)				−0.64**				0.52*			−0.50**	−0.65**
Striped bass (FMWT index)	0.68**			0.81**		0.51*			0.63**			0.72**
Yellowfin goby (FMWT catch per tow)	−0.34		0.39*				−0.52*				0.53**	
Starry flounder (FMWT catch per tow)	0.34	0.41*		0.60**	−0.67**	−0.49*		−0.75**	0.59**	0.53**	0.33*	0.70**
Crappie (relative abundance)										0.54**		0.39
Sunfish (relative abundance)	−0.50**	0.33		−0.63**					−0.40*	0.57**		−0.48*
Largemouth bass (relative abundance)	−0.40**		0.40*	−0.64**	0.41			0.44	−0.41*	0.36		−0.52*
Silversides (relative abundance)	−0.53**			−0.68**				0.58*	−0.52*			−0.66**

All parameters were log-transformed. For each data series, the first column shows the correlations of the original data (log-transformed), the second column shows the correlations of the trend stationary data, the third column shows the correlations of the difference stationary data, and the fourth column shows the correlations of the data transformed as three-year backward moving averages. The correlations are for the entire time series. Only values for $p < 0.10$ are shown; values that are significant at $p < 0.05$ are indicated by *, and those significant at $p < 0.01$ are indicated by **. Negative correlations are highlighted in blue, and positive correlations are highlighted in pink ($p < 0.05$ [lighter shade] and 0.01 [darker shade] only).

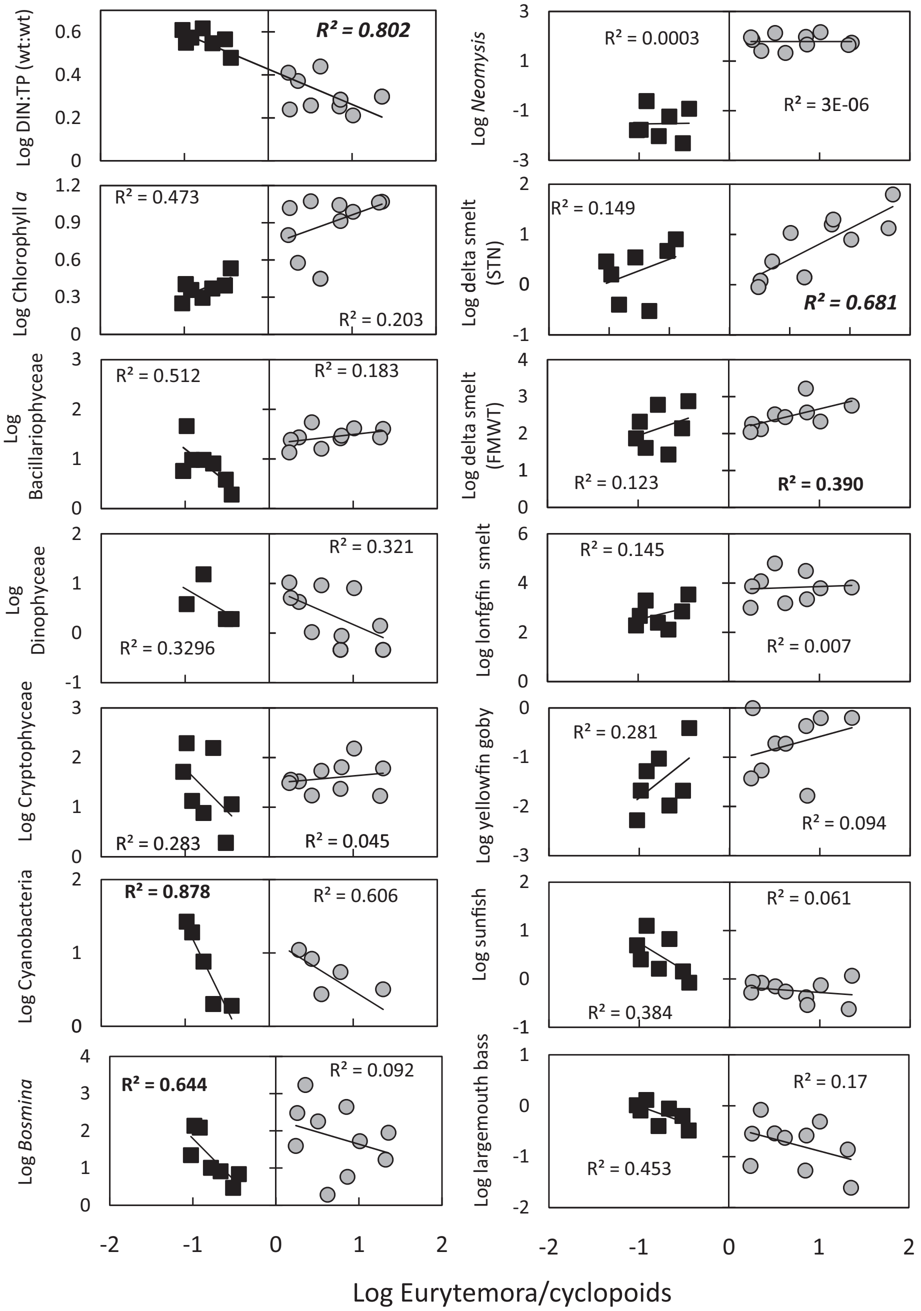

Figure 24 Comparison of abundance of the major groups of phytoplankton, zooplankton, and fish as a function of the *Eurytemora affinis*/cyclopoid ratio for two periods of the time course: 1975–1986 (●) and 1999–2005 (■). These time periods represent the beginning years of the time course and the years encompassing the POD. Among the significant relationships are those of the *Eurytemora affinis/*cyclopoid ratio and the DIN: TP ratio, cyanobacteria, *Bosmina*, and delta smelt (STN or FMWT data) (p <0.05).

Egeria has been identified as an "ecological engineer" (Yarrow et al., 2009; sensu Jones et al., 1994). As its coverage increases, it affects nutrients via uptake, decreases turbidity by sediment trapping, increases light availability, and is also thought to positively affect zooplankton by providing a refuge from predation (Figure 25). As these beds trap sediments, they also alter water flow (Gacia and Duarte, 2001; Wetzel, 2001). In the Bay Delta, decreased turbidity has been noted in macrophyte areas (Hestir et al., 2010). Higher abundance of macro-suspension feeders, including bivalve molluscs, also generally occurs in vegetated areas. As summarized by Marba et al. (2006), this is due to "enhanced rates of recruitment within canopies (Duggins et al., 1990; Boström and Bonsdorff, 2000), shelter from predation (Peterson and Heck, 2001) and

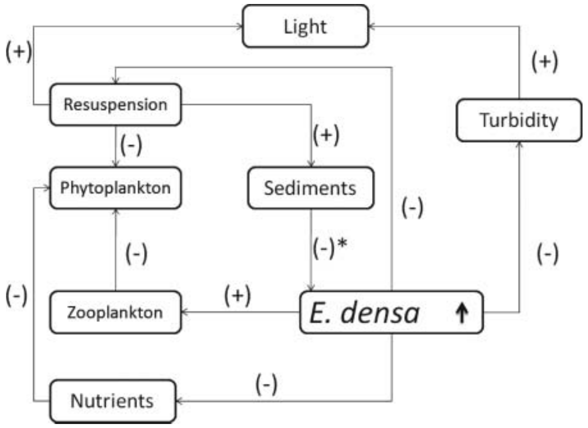

Figure 25 Schematic depiction of *Egeria densa* as an "ecosystem engineer." As *Egeria* increases, turbidity decreases, and light increases, Also, nutrients are taken up by the plants (but may be mobilized from the sediment; see text). Zooplankton increases due to the ability to find refuge from predation, but phytoplankton decrease due to zooplankton grazing. Figure reproduced from Yarrow et al. (2009) with permission.

high abundance of food availability." The extent to which invasive, structurally complex species alter habitat—and therefore food webs—is a function not only of their biomass, but also the extent to which they replace other structurally complex submersed macrophyte species or add new structure to an otherwise more open habitat (Martin and Valentine, 2010).

Macrophyte beds provide habitat for largemouth bass. These fish nest among the submersed vegetation (Moyle, 2002). In the Bay Delta, largemouth bass are increasing (Figure 19), and this increase has been linked to the habitat provided by beds of *Egeria* (Conrad et al., 2010). Brown and Michniuk (2007) documented an increase in alien centrarchids in macrophyte habitats in recent years as well, compared to surveys of decades past. From a stoichiometric viewpoint, *Egeria* biomass differs from that of the dominant fish that thrive in these beds; published stoichiometry data of *Egeria* suggest a plant that has a high N:P content (Yarrow et al., 2009), while the dominant fish would be expected to have a low biomass N:P ratio.

Summary of Part II

Patterns in the abundance of various members of the aquatic community in the Bay Delta, from phytoplankton and macrophytes to zooplankton, invertebrates, and fish follow trends predicted by ecological stoichiometry theory. Members of different trophic levels were found to have different correlations with N and P, as did taxa within trophic levels. These patterns are consistent with the general premise that the fish community becomes proportionately more P-rich with increasing levels of consumers (Sterner and Elser, 2002). The patterns are also consistent with the increased development of a benthic food web following reduction in P loading. The comparisons of trends in taxa based on original versus detrended data illustrates that the most significant relationships with nutrients were robust even when autocorrelation was removed (an expected result since most parameters did not have significant autocorrelation).

PART III: ECOLOGICAL STOICHIOMETRY AND BIOGEOCHEMICAL INTERACTIONS

Ecological stoichiometric principles, and the data described above, suggest that there is a negative relationship between ambient levels of P in the environment and the abundance of piscivorous or omnivorous fish. As described above, such fish have higher metabolic and structural demands for P in their biomass than do smaller, more planktivorous fish and, thus, may be more efficient at sequestering the needed element. However, these large fish increased when P loads were reduced, leading to elevated N:P in the water column. The question arises: *What is the source of the P that supports these fish?* These organisms may be efficient at sequestering the needed element, but it must be available in order to be taken up. The related questions are thus: *To what extent are nutrient biogeochemical processes altered when the stoichiometry of land-based sources changes? What nutrient feedbacks may help to sustain an altered ecosystem structure?* From a stoichiometric perspective, altered biogeochemical pathways serve to provide the mechanism whereby nutrient dynamics supporting trophodynamics are changed. A stoichiometric perspective also suggests that altered biogeochemical pathways may shift environments so as to make them more conducive to the success of different species, some of which may be invasive. The hypothesis posed here is that through alterations in nutrient loads and resulting biogeochemical changes, the Bay Delta became a conducive environment for the invasion of *Egeria* and, in turn, *Corbula* and *Microcystis*.

Years of nutrient loading may result in large sediment reservoirs of nutrients for a considerable time (years) after the rate of loading is reduced (Chapra and Canale, 1991; Wetzel, 2001; Carpenter, 2005). Sediment chemistry measurements in estuaries show that concentrations of nutrients in the sediments are significantly higher than in the water column. Sediments represent enormous stores of both P and N; porewater NH_4^+ concentrations have been documented to reach up to 1 mM (= 14 mg L^{-1}) and PO_4^{3-} more than 50 μM (= 1.6 mg L^{-1}) in a wide range of environments (e.g., Udy and Dennison, 1997; Touchette and Burkholder, 2000 and references therein; Figure 26). In the Bay Delta, where P has been measured in the upper few cm of sediment, concentrations were 5–10 μmol g^{-1} in the confluence region but significantly higher in the more freshwater sites when samples were collected in fall of 2001 (Nilsen and Delaney, 2005). Locked in sediments as mineral or strongly adsorbed species, much of the P is not biologically available. In freshwater systems (Carlton and Wetzel, 1988; Wetzel, 2001) as well as marine habitats, several biogeochemical and chemical processes mobilize this P, making it available for organismal uptake. These abiotic and biotic processes are described below,

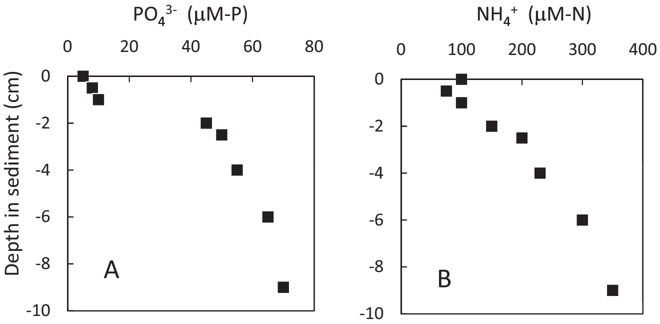

Figure 26 Pore water profiles of PO_4^{3-} and NH_4^+ from May 2004 at Freestone Point on the Potomac River, Chesapeake Bay, USA. This figure illustrates the main characteristics of Potomac River pore water chemistry. Data are from Bailey et al. (2006).

followed by a description of the interactions of altered geochemical and biogeochemical processes as they affect the food web.

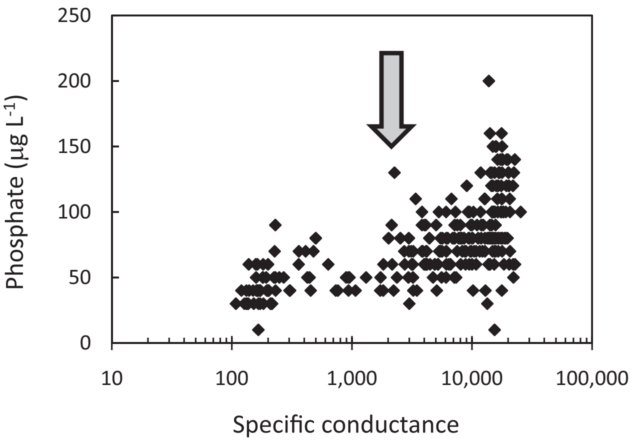

Figure 27 Relationship between the concentration of PO_4^{3-} (μg L^{-1}) and the specific conductance (μmhos cm^{-1}). Data shown are bimonthly averages for the time series for station D8 located near Suisun Bay. The arrow indicates the conductance approximately equal to a salinity of 2.

Abiotic Release of P from Saltwater Intrusion

In non-calcareous freshwater sediments, P is most often bound to iron oxyhydroxides (FeOOH) (Compton et al., 2000; Jordan et al. 2008). The FeOOH-bound P may be delivered to estuaries with transport of suspended solids, or it may become adsorbed to particulates when P is discharged from other sources, such as from point source discharges. When this bound P meets saline or/and sulfate-rich water, either from transport down-estuary or from salt intrusion to sediments, the formation of iron sulfide minerals releases P to the overlying water (Caraco et al., 1989; Jordan et al., 2008; Lehtoranta et al., 2009). The sulfides produced in saline sediments preferentially bind with the Fe, releasing P and precipitating Fe(II); this has been termed the iron conveyer belt (Jordan et al., 2008). A simplified representation of the net process is

$$\mathrm{FeOOH(s)} \cdot \mathrm{H_2PO_4^-}\ \mathrm{(ads)} + \mathrm{H_2S} \rightarrow \mathrm{FeS\ (s)} + \mathrm{H_2PO_4^-}\ \mathrm{(aq)}, \tag{1}$$

where (s) refers to solid phase, (ads) refers to adsorbed, and (aq) refers to aqueous. In freshwater, FeOOH-bound P may be released under anoxic conditions, but the cycle of Fe binding of P begins anew when oxygen is encountered again (Carignan and Flett, 1981). In the Bay Delta, high concentrations of Fe-bound P in sediments have been reported (Nilsen and Delaney, 2005).

This "iron conveyor belt" has been demonstrated in studies of P fluxes in the Patuxent River Estuary, a tributary of Chesapeake Bay (Jordan et al., 2008). There, Fe-bound P was found to decline with increasing salinity. Furthermore, highest concentrations of dissolved P in river transects were found in the region of the river where salinity ranged from ∼2–4. When PO_4^{3-} concentrations for the Bay Delta are plotted as a function of specific conductance for all data available in the 30-year record for a station just outside Suisun Bay (Figure 27), an increase can clearly be seen. Thus, as salinity moves inland, more P is released from the sediments. The drier the season or year, the more P should flux from the sediment; the wetter the season or year, the smaller this flux.

In Tomales Bay, California, USA, Chambers et al. (1995) estimated that release of PO_4^{3-} from Fe-bound P was ∼12% of the benthic flux of P in sediments that were sulfide rich. In the Patuxent Estuary, release from iron oxides was estimated to contribute ∼30% of dissolved PO_4^{3-} to the estuary, with point source discharges contributing another 50–60%. The contribution of this flux is highest in summer when rates of $SO_4{}^{-2}$ and Fe(III) reduction are highest (Boynton et al., 1995, 2008; Jordan et al., 2008).

Salinity has an opposite effect on N fluxes compared to P fluxes. Whereas P flux rates are higher in saltwater, rates of NH_4^+ flux are higher in freshwater (Jordan et al., 2008 and references therein), and this can accentuate the discrepancy between N:P ratios along the salinity gradient. Consistent with this idea, one study was conducted on benthic fluxes of nutrients in the upper Bay Delta in late summer, and rates of PO_4^{3-} efflux ranged from insignificant to ∼0.06 mmole $m^{-2}d^{-1}$, considerably lower than rates previously found for the more saline reaches of the estuary and considerably lower than those of NH_4^+ (Kuwabara et al., 2009). Comparisons of the NH_4^+: PO_4^{3-} ratio along the salinity gradient of four sub-estuaries of the Chesapeake Bay (Patuxent, Potomac, Choptank, and Bush Rivers) revealed a common switch from molar ratios >16 to <16 as salinity increased, with a major breakpoint in the salinity range of 1–4 (Hartzell and Jordan, 2010). Seitzinger et al. (1988) suggested that lower denitrification efficiencies in saltwater compared to freshwater arise, at least in part, due to decreased adsorption of NH_4^+ at higher ionic strengths, which leads to poor efficiency of nitrification. Regardless of salinity, the supply of labile organic matter to sediment remains a key determinant of sediment N fluxes.

Biota-Mediated P and N Fluxes

Abiotic processes are significant, but they are not the only pathways by which P and N may be mobilized into solution. Macrophytes such as *Egeria* take up nutrients from the sediment and the water column; the relative importance of these two sources depends on the ambient concentrations in each (Moeller et al., 1988; Wetzel, 2001; Feijoo et al., 2002). *Egeria* has a high N:P content (Yarrow et al., 2009) and has the physiological capability to balance its N demand by water-column uptake and its P demand by sediment uptake in waters with high N:P ratios. Classic work by Barko and Smart (1980) showed that PO_4^{3-} turnover in the interstitial water increased 1,000-fold in sediments supporting Eurasian milfoil or *Egeria* growth. *Egeria*, and the related invasive macrophyte hydrilla, can attain high biomass levels and very high growth rates. In dense, productive stands, the environment for these two submersed plants can become limited by free CO_2, but both species have well-developed C-concentrating mechanisms (Bowes, 1987; Bowes and Salvucci, 1989; Lara et al., 2002; Pierini and Thomaz, 2004). In a (relatively) closed system, CO_2 (aq) depletion during photosynthesis increases pH, and the dissolved inorganic C system shifts toward increased dominance of $HCO_3{}^-$:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \quad (2)$$

Hydrilla and *Egeria* are able to use $HCO_3{}^-$ efficiently with the consequence of elevating the pH of the surrounding water. In fact, hydrilla, while capable of growing well across a pH of 5–9, has a ten-fold higher growth rate at pH 9 than in lower pH conditions (Spencer and Bowes, 1986; Bowes, 1987). Thus, the elevated pH from high productivity has a positive effect on growth rate of these plants. Conversely, low pH and/or increases in sulfate, which also reacts with $HCO_3{}^-$, have been shown to be detrimental to *Egeria* (Mulsow and Grandjean, 2006).

Although measurements of pH for the Suisun Bay region have not been taken regularly over the time series of interest, long-term general trends in pH at a range of stations in the Bay Delta show similar patterns, including an increase since the mid-1990s (Figures 28A,B). High-frequency measurements show a diel oscillation with late-day pH elevations during the summer growing season (Figure 28C), and pH values > 10 have been recorded in the western Delta (Lindemuth, 2010).

As pH increases, the fundamental physical–chemical relationships related to P adsorption–desorption change. Enhancement of sediment P release under elevated water-column pH conditions has been observed in eutrophic lakes (i.e., Andersen, 1974; Drake and Heaney, 1987; Jensen and Andersen, 1992; Xie et al. 2003) and tidal freshwater/oligohaline estuaries (Seitzinger, 1991). For example, PO_4^{3-} flux from the sediment in the Potomac River increased from <5 μmol m^{-2} h^{-1} to nearly 30 μmol m^{-2} h^{-1} in <24 hr when the pH increased from 7.8 to 9.5 (Figure 29). The effect of pH 10.5 is far greater, however, as PO_4^{3-} efflux increased to > 100 μmol m^{-2} h^{-1} in 24 hr and continued to increase to > 160 μmol m^{-2} h^{-1} when these high

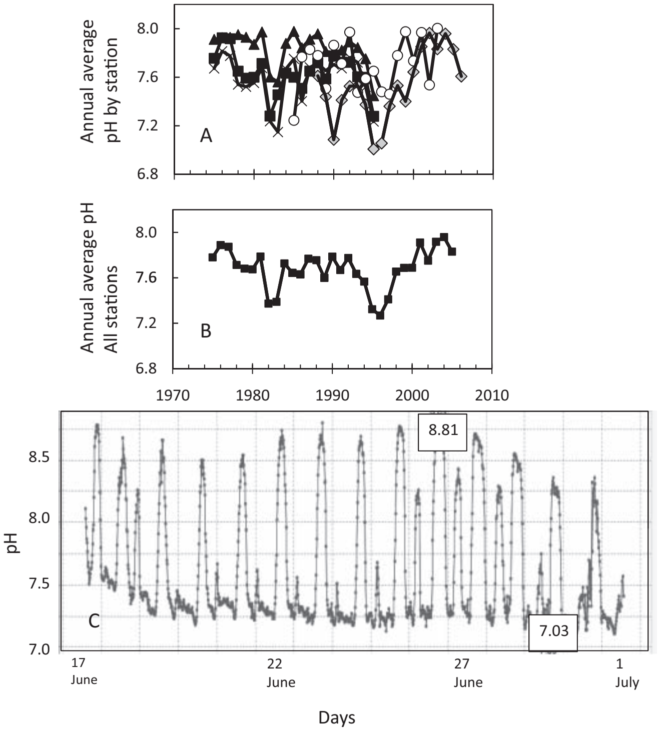

Figure 28 (A) Annual average pH for various stations (from Suisun Bay to lower San Joaquin and upper Sacramento River) in the Bay Delta over time, (B) mean of annual average pH of these stations over time, and (C) snapshot of diel fluctuations in pH from 17 June 2009 to 1 July 2009 in the Grantline Canal, as measured from an in situ pH data sonde. Data are from http://bdat.ca.gov (panel A) and http://cdec.water.ca.gov/ (panel C).

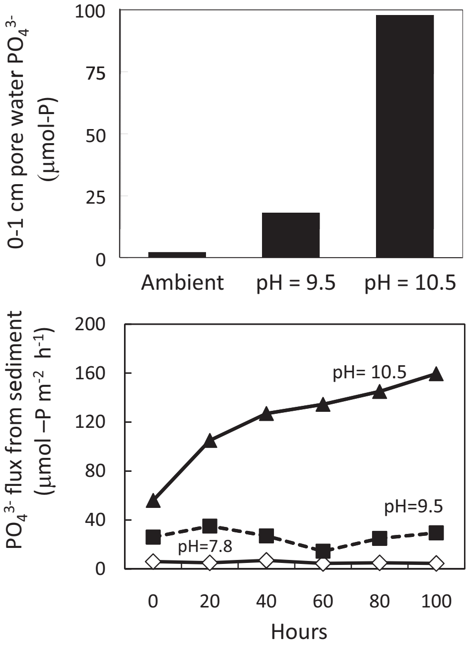

Figure 29 Change in rate of flux of PO_4^{3-} from cores taken from a *Hydrilla*-dominated reach of the Potomac River, Chesapeake Bay, USA, and experimentally manipulated to alter the pH (data from Bailey et al. 2006).

pH values were sustained for 100 hr (Figure 29). Organisms that can tolerate high pH and high NH_4^+ (such as *Egeria*) thus form the base of the food web in these stands. In turn, their metabolism affects the availability of benthic PO_4^{3-}. Rates of release of P from *Egeria* stands in Arkansas, USA, have been estimated to range from 0.13 to 0.36 μM L^{-1} d^{-1} for a stand corresponding to 132 cm^2 of plant area and a density of 788 g m^{-2} (Arnott and Vanni, 1996, based on data from Barko and Smart, 1980).

In summary, benthic sources of P are mobilized and can support the food web through two important mechanisms: salt intrusion resulting in localized abiotic exchange, and elevated pH resulting from highly productive macrophyte communities. Increased production in *Egeria* stands, which promote increased pH over diel cycles, may provide an important mechanism whereby P becomes available, and this can, in turn, fuel other components of the benthic food web.

Altered Biogeochemical Processes and Effects under Conditions of High Benthic Primary Productivity

Several other biogeochemical pathways are altered when pH is elevated due to highly productive benthic macrophytes under such conditions: First, elevated pH resulting from high productivity by macrophytes affects the biogeochemical cycling of N, including the chemistry of NH_4^+-NH_3 and processes such as nitrification, denitrification, and dissimilatory $NO_3{}^-$ reduction to NH_4^+ (e.g., Huesemann et al., 2002; Kemp et al., 2005). The form of NH_4^+-NH_3 is a function of pH based on the reaction

$$NH_3 + H_2O \xleftrightarrow{K_b} NH_4^+ + OH^-, \tag{3}$$

where K_b is the equilibrium constant (Bange, 2008). At elevated pH, the proportion of NH_3 to $\Sigma(NH_3 + NH_4^+)$ increases; the salinity dependence of K_b results in an increase in the proportion of NH_3 at lower pH under freshwater conditions than under brackish/marine conditions. Moreover, at high pH, direct volatilization of NH_3 from *Egeria* has been observed (Reddy et al., 1987).

Elevated pH also alters bacterial metabolism (Tank et al., 2009). Both bacterial production and respiration can be negatively affected by alkaline pH resulting from high rates of macrophyte photosynthesis, which, in turn, affects C cycling and energy flow and reduces rates of remineralization (Tank et al., 2009). The bacteria *Nitrosomonas* and *Nitrobacter* are inhibited by NH_3, and their inhibition, in turn, reduces nitrification. Without nitrification, elevated NH_4^+ and NH_3 are sustained (Russo, 1985; Kemp et al., 2005). Increasing NH_4^+ shifts aquatic communities to dominance by phototrophs with higher NH_4^+ tolerance, for example, dinoflagellates and macrophytes such as *Egeria*. As NH_4^+ increases, organisms that tolerate it increase; as primary production increases, pH increases, and the equilibrium shifts to NH_3. Feedback inhibition of the food web may occur due to the toxic effects of NH_3. There are multiple physiological effects to exposure to high NH_3 levels. Shrimp, for example, alter their ability to osmoregulate, with the degree of disruption a function of both concentration and exposure time (Lin et al., 1993). Values of pH > 9.7 have also been found to be lethal for some shrimp species (Shaw, 1981). Toxic effects of unionized NH_3 on fish are multi-faceted and can include damage to the gill epithelium, stimulation of glycolysis and suppression of the Krebs cycle, uncoupling of oxidative phosphorylation and inhibition of ATP production, disruption of osmoregulation and effects on liver and kidneys, and suppression of the immune system, leading to susceptibility to infection (Tomasso et al., 1980; Alabaster and Lloyd, 1982; Russo, 1985; Adams and Bealing, 1994; Camargo and Alonso, 2006). Collectively, these effects can lead to reduced feeding activity, fecundity, and survivorship (Alonso and Camargo, 2004).

Toxic effects of NH_4^+ and NH_3 on the common calanoid copepods, *Eurytemora* and *Pseudodiaptomus*, have been reported in the Bay Delta (Flores et al., 2010). For example, *Pseudodiaptomus* reproduction rates are negatively affected, as are nauplii and juvenile growth rates (Flores et al., 2010). Both taxa are negatively correlated with NH_4^+ in the long-term data (Table 4). Suppression of productivity and reduction in the proportion of primary productivity and bacterial productivity have been reported for other N-hypersaturated systems as well (Waiser et al., 2011), and such impacted systems have been identified as significant sites of ecological change (Brooks et al., 2006).

Macrophyte production can also alter the biogeochemistry of calcification by increasing the pH, and macrophytes alter sediment $CaCO_3$ dissolution rates through aerobic respiration (Burdige and Zimmerman, 2002). The pK of calcium carbonate is 7.9. As the pH rises, the reaction

$$Ca(HCO_3)_2 \leftrightarrow CaCO_3 + H_2CO_3 \tag{4}$$

is driven to the right, thus increasing calcification. In macrophyte communities, calcifying fauna often represent the dominant epibiota (Marba et al., 2006). These fauna are preferred sources of food for fish, such as sunfish (e.g., Werner and Hall, 1979; Schramm and Jirka, 1989; Toft et al., 2003). Larger organisms with more bone also have a greater need for Ca than do smaller organisms; shad, for example, increase their Ca in biomass from 1 to 6% when their length increases from 20 to 120 mm (Pilati and Vanni, 2007).

In addition to changes in availability of epiphytic biota, bivalve molluscs are important calcifiers. The precipitation of $CaCO_3$, a complex process in bivalves, requires significant PO_4^{3-} as well as Ca^{2+} (Asana and Ito, 1956). TP requirements in shellfish are high (Asano and Ito, 1956); in fact, in a comparison of net incorporation rates of P in fish and shellfish, those of the shellfish were higher (Asana and Ito, 1956). Concentrations of Ca^{+2} in sediment porewater in areas occupied by clams would be expected to be much higher than in sediments where clams are not abundant. In addition to metabolic fluxes, shell dissolution from dead clams can contribute to such concentrations and help to sustain elevated Ca^{+2} concentrations in a positive feedback.

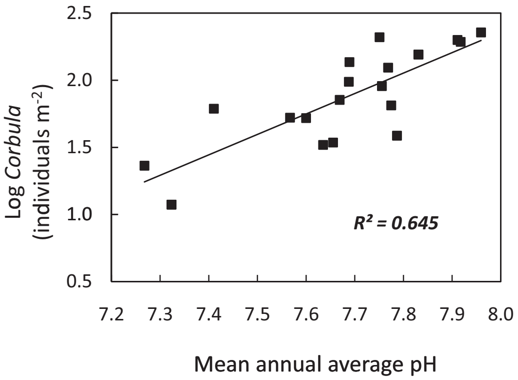

Figure 30 Annual abundance of *Corbula amurensis* (log of individuals m^{-2}) at stations located from the confluence to Suisun Bay in relation to mean annual average pH. Coefficient of determination (R^2) was significant at $p < 0.01$.

As shown above, in the Bay Delta, there is a strong long-term correlation between water-column DIN:TP ratios (and DIN:PO_4^{3-} ratios) and abundance of the clam *Corbula* (Figure 18, Table 5) (Glibert, 2010). There is also a strong long-term positive relationship between pH and *Corbula* abundance (Figure 30). This species invaded the Bay Delta in 1987 at the start of a several-year drought (Alpine and Cloern, 1992; Kimmerer, 2004). Some freshwater bivalves appear to be particularly well adapted to sustain drought and dry periods, and such adaptations relate, as well, to Ca metabolism. *Corbula* spp. burrows a few centimeters into the sediment, with at least a portion of its siphon remaining in the water column. This animal has a pelagic larval stage that is typically in the water column for several weeks in spring, and it accelerates rates of calcification in summer when temperature and pH are elevated (Hrs-Brenko, 2006).

Biological and Biogeochemical Feedbacks and Microcystis *Abundance*

Positive feedback mechanisms thus exist between macrophyte production, pH, nutrient efflux, and calcification. Additional positive feedback interactions between clam production, excretion, altered biogeochemical processes, and nutrient accumulation help to explain why shifts in algal assemblage composition occur when clams are abundant (Glibert, 2010). Although cyanobacteria increased in abundance in the mid-1980s, the abundance of *Microcystis* has escalated significantly in the past decade (Lehman et al., 2005, 2008, 2010). *To what extent might the increase in* Microcystis *in the Bay Delta be a consequence of such positive feedbacks?*

Numerous studies have suggested a linkage between the increased prevalence of cyanobacteria blooms and either reduced stocks of planktivorous fish (e.g., Reinertsen et al., 1986; Hessen, 1997) or increases in invasive bivalve molluscs (e.g., Bykova et al., 2006). Both trophic cascade effects and altered nutrient cycling from changes in nutrient release have been thought to be the linking mechanisms. Nutrient loading can interact with resource removal through trophic cascading. Depletion of large grazers (including invertebrates) results in decreased predation on macro- and microzooplankton, leading to reductions in microzooplankton populations and increases in algal blooms in the nutrient-enriched environment (Merrell and Stoecker, 1998; Stibor et al., 2004; Vadstein et al., 2004). In cyanobacteria-dominated reservoirs in Australia, a trophic link between mesozooplankton and *Cylindrospermopsis* has been suggested (Ying et al., 2010). Mesozooplankton preferentially consume algae other than *Cylindrospermopsis*, in turn releasing P that is rapidly taken up by the cyanobacteria. This phenomenon may be germane with respect to increases in *Microcystis* blooms, not only in the Bay Delta but also in many other systems affected by invasive species. *Microcystis* is also a superior algal competitor under elevated pH; like *Egeria*, it has highly effective C-concentrating mechanisms, allowing it to sustain photosynthesis when other algae become C-limited (Jähnichen et al., 2007 and references therein).

Links between zebra mussels and *Microcystis* have been examined in various systems (discussed below; Sarnelle et al., 2005), and these findings may be analogous to the relationship between invasive clams and *Microcystis* in the Bay Delta. Excretion is significantly higher by zebra mussels than by crustacean zooplankton (Conroy et al., 2005). Ecological stoichiometric principles have been examined with respect to zebra mussel invasions of lakes in Sweden (Naddafi et al., 2009). While nutrient stoichiometry was not directly linked to mussel fitness, zebra mussels tolerated low P, and their stoichiometry was altered by both food quantity and quality.

Toxin production by *Microcystis* provides yet another positive feedback. Cyanotoxins, such as microcystins, appear to adversely affect growth and development of daphnids, with offspring of toxin-exposed daphnids showing decreased growth and survival even if they were subsequently raised in microcystin-free conditions (Dao et al., 2010; Ortiz-Rodríguez and Wiegand, 2010). Wang et al. (2010) showed that *Microcystis* developed in experimental systems when zooplankton were included, but not in enclosures where zooplankton were removed prior to the experiment. *Microcystis* blooms in lakes typically occur when small-sized zooplankton dominate (Allan, 1977; Edmondson and Litt, 1982; Wang et al., 2010). The effect of microcystins on *Daphnia* in the Bay Delta has not been examined, but in laboratory experiments with copepods, more detrimental effects have been observed on *Eurytemora* than on *Pseudodiaptomus* (Ger et al., 2010).

Various studies have related increasing N and increasing N:P ratios to increased toxicity of *Microcystis*. In the Daechung Reservoir, Korea, *Microcystis* toxicity was related not only to an increase in N in the water but also to cellular N content (Oh et al., 2001). In P-limited chemostats, Oh et al. (2000) observed that while *Microcystis* growth declined as P limitation increased, more microcystins were produced. In addition, the more toxic form, microcystin-LR, was produced compared to microcystin-RR (Figure 31). Excess N has also been related to microcystin production under controlled culture conditions (e.g., Lee et al., 2000; Vézie et al., 2002; Downing et al., 2005;

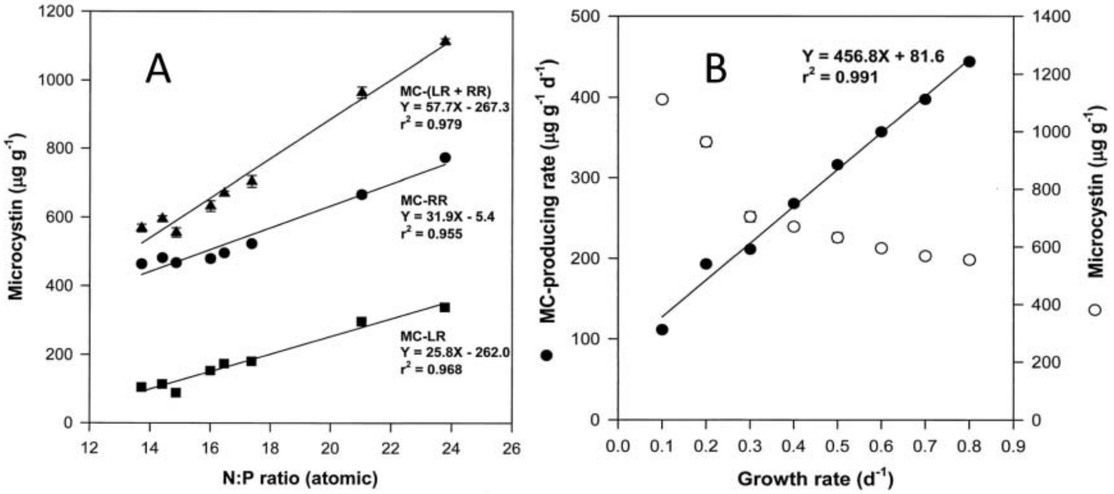

Figure 31 (A) Relationship between the N:P atomic ratios and the concentrations of different microcystin toxins (MC-LR, MC-RR, and MC-[LR + RR]) of *Microcystis aeruginosa* grown in laboratory P-limited cultures. (B) The microcystin-production rate (●) and microcystin content (○) of *M. aeruginosa* at each growth rate in laboratory P-limited cultures. Figure reproduced from Oh et al. (2000) with permission.

Van de Waal et al., 2009). In the Philippines, increased *Microcystis* was associated with high N loading but not P loading, and its cellular P content (cell quota) was low (Baldia et al., 2007). In the Huron River, Michigan, USA, *Microcystis* has been associated with molar water-column N:P ratios ranging from 40 to 80 (Lehman, 2007). Similar relationships were reported for a field survey of Hirosawa-no-ike Pond, Kyoto, Japan; the strongest correlations between microcystins and nutrients were found at high concentrations of NO_3^- and NH_4^+, and seasonal bloom maxima occurred at high water-column N:P ratios ranging from 40–90 (Ha et al., 2009). In both field studies and in culture, the molar cellular N:P ratio of *Microcystis* has varied from ∼10 to more than 30 (Tsukada et al., 2006). Thus, both abundance and toxicity of *Microcystis* appear to be enhanced under high water-column N:P ratios. This would suggest that *Microcystis*, unlike many phytoplankton, does not follow the "you are what you eat" stoichiometric model (Sterner and Elser, 2002, p. 16), but instead functions stoichiometrically more like a heterotroph, in this case, sequestering P and potentially releasing excess N in the form of the toxin microcystin. It may also have the capability to reduce its P requirement by lipid substitution, as shown for other cyanobacteria (Van Mooey et al., 2009). From its C-concentrating capability (Jähnichen et al., 2007) to its P metabolism and its tolerance and/or preference for NH_4^+, *Microcystis* appears well adapted to the present environment of the Bay Delta where pH values fluctuate and can become elevated on episodic bases and where N:P ratios have increased over time.

Broad surveys have been undertaken to assess relationships between cyanobacteria and water-column N:P ratios. Some of these have included all cyanobacteria (including the N_2-fixing species), others only *Microcystis*. For example, Downing et al. (2001) examined data from 99 lakes from around the world and reported that TP or TN were better predictors of cyanobacteria than N:P ratios. Others have shown that low N:P ratios can favor cyanobacteria (e.g., Smith, 1983; Stahl-Delbanco et al., 2003). *Microcystis* can tolerate elevated N:P ratios, and thus, its dominance under high N:P ratios may also reflect the decline in other species that lack such tolerance. Cyanobacteria do not have to grow faster at elevated N:P than at lower N:P values to become abundant; they merely have to grow faster than competing species groups (Glibert, 2010). Clearly, there is great plasticity in the ability of cyanobacteria to grow in a wide range of environments, including elevated N:P environments.

Summary of Part III

Conceptually, the relationships examined between changes in pH and altered salinity and the major biogeochemical processes are summarized in Figure 32, while the changes over time and the shift in dominant biogeochemical processes are depicted in Figure 33. While the interactions among the biogeochemistry and biology and their changes over time are complex, the important point is the interconnectedness of these relationships. Changes in external nutrient loads can drive changes in internal ecosystem biogeochemistry and, in turn, trophodynamics. This analysis suggests that increasing dominance over time of macrophytes, clams, and *Microcystis*, along with more omnivorous fish that are fueled by a benthic food web, are not a result of stochastic events (random invasions) but, rather, are related to a cascade of changes in biogeochemistry resulting from changes in nutrient loading over time as a major driver. This analysis supports the premise that reductions in P loading from external sources drive aquatic systems toward increased importance of sediment dynamics and toward the sediments as a major source of P. The food webs that are supported are different from those supported when the water column is the major source of P; they are benthic-dominated. Macrophytes, such as *Egeria*, and phytoplankton, such as *Microcystis*, are

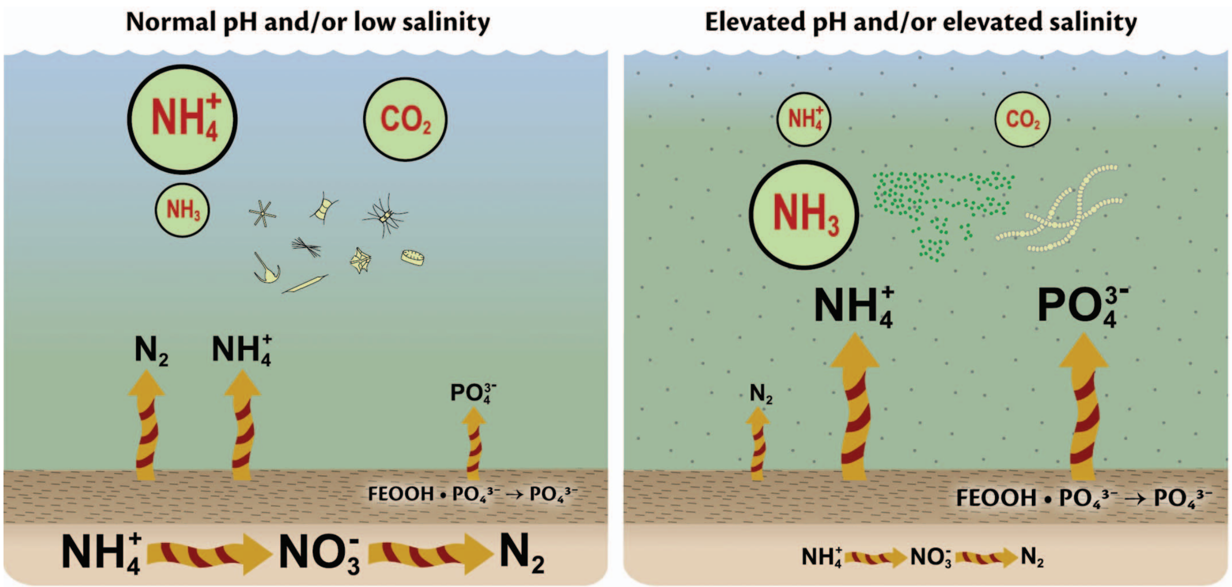

Figure 32 Conceptual diagram of the effect of altered pH and altered salinity on the processes of exchange of PO_4^{3-} and NH_4^+ from the sediment to the water column. With a rise in pH, or a shift to higher salinity, the sediment flux of NH_4^+ and $PO4^{3-}$ increases via the mechanisms described in text. pH also alters the equilibrium between NH_4^+ and NH_3, leading to higher NH_3 at high pHs (color figure available online).

physiologically well adapted to these altered nutrient and pH regimes. The communities of bivalves and fish change accordingly.

PART IV: COMPARATIVE ECOSYSTEMS

Many systems show commonalities with respect to impacts of eutrophication (reviewed by Cloern, 2001). The changes over time in the Bay Delta have been described as uniquely complex, driven primarily by the wide range in effects of invasive species and alterations in habitat (e.g., Alpine and Cloern, 1992; Bennett and Moyle, 1996; Cohen and Carlton, 1998; Kimmerer, 2004). This notion of unique complexity for the Bay Delta is not supported, however, by the following comparison with other aquatic systems undergoing stoichiometric changes in nutrient loads. Here, comparisons of other ecosystems are made with the Bay Delta in terms of (1) changes in state from a system with high chlorophyll *a* and high pelagic productivity to one dominated by macrophytes when P was reduced; (2) invasions of bivalves following P removal; (3) associations between high macrophyte production, invasive bivalves, piscivorous fish, and *Microcystis* growth, and/or (4) reductions in invasive species following targeted nutrient reduction measures. These comparisons illustrate a similarity in the timing of P reductions and the susceptibility of these systems to invasions by macrophytes and bivalves.

Lake Washington

A classic example of a system that has sustained shifts to new stable states following P removal is Lake Washington. This large, deep lake is surrounded by the city of Seattle, Washington, USA, and was historically degraded by major inputs of secondary-treatment sewage from the 1940s to the early 1960s (Edmondson, 1996). In the 1960s, Seattle and the surrounding communities adopted zero sewage discharge policies for the lake (except for combined sewer overflows; Krebs, 2008). Diverting most sewage away from Lake Washington caused N:P ratios to increase (Figure 34). By 1970, phytoplankton growth had decreased to levels that had not been seen since the early 1950s, including a major decline of the filamentous cyanobacterium *Planktothrix* (*Oscillatoria*) *rubescens* that had bloomed in the P-rich conditions (Edmondson and Lehman, 1981; Hampton et al., 2006). Zooplankters such as "keystone herbivores" *Daphnia* spp. became increasingly abundant (Edmondson and Litt, 1982; Winder and Schindler, 2004a,b), while their major predator, the macrozooplankter *Neomysis mercedes*, declined rapidly (Eggers et al., 1978; Edmondson and Litt, 1982). Longfin smelt were abundant in the early 1960s but also declined (Hampton et al., 2006). Although the food web interactions are complex in this lake (Hampton et al., 2006), and other influences such as climate change have been linked to these changes (Winder and Schindler, 2004a,b), the declines in chlorophyll *a* and *Neomysis*, as well as the increase in *Daphnia* following P removal and N:P increases, are consistent with those of the Bay Delta.

Potomac River, Chesapeake Bay

The Potomac River has undergone many similar changes to those in the San Francisco Estuary (Figure 35, Table 7), some of which differ from those of the Chesapeake Bay as a whole, since the Potomac is most directly influenced by nutrient

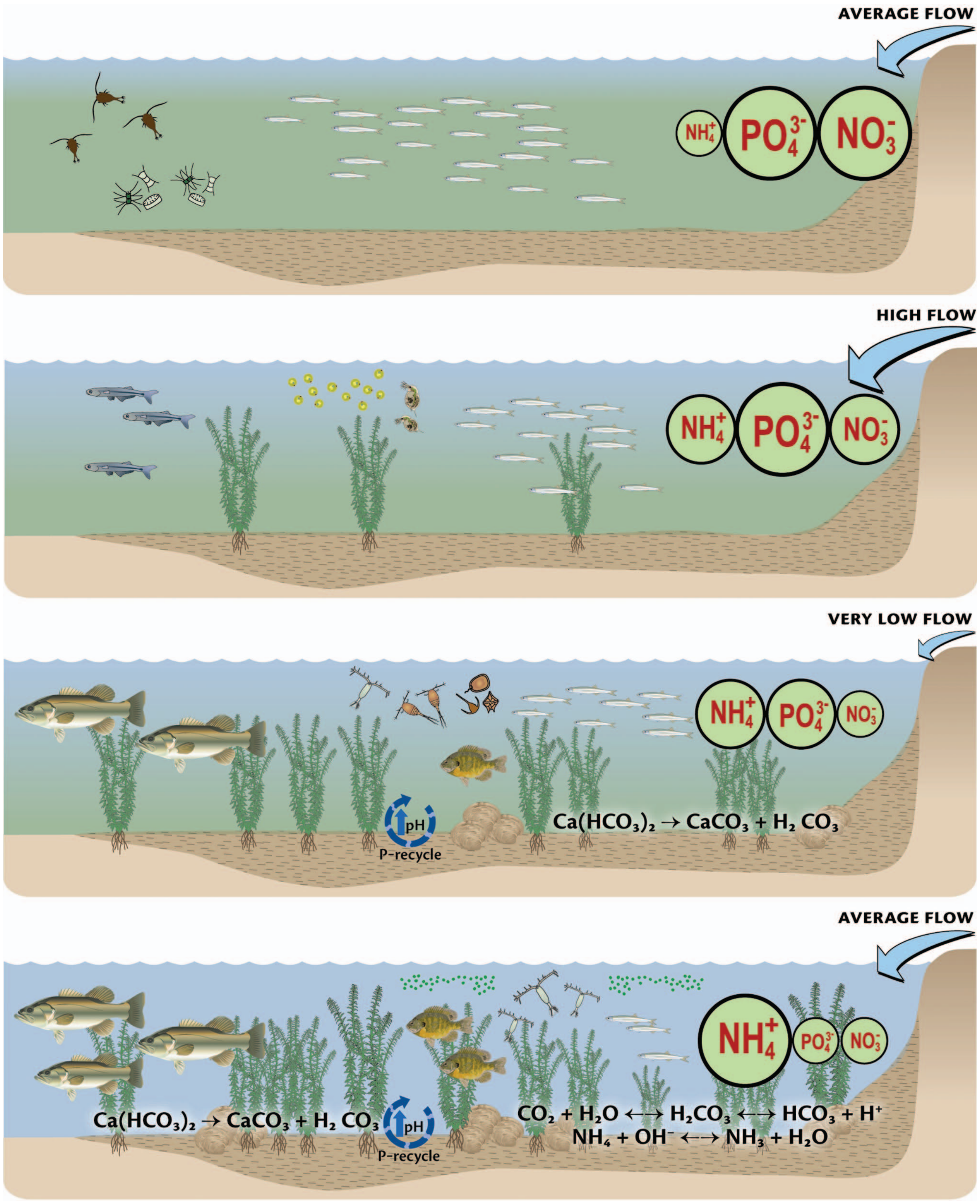

Figure 33 Conceptual depiction of the change over time in major nutrients, flow, dominant biogeochemical processes, and the food web of the Bay Delta. The first panel represents the period from 1975 to ∼1982 when flow was low, and diatoms and *Eurytemora* were the dominant phytoplankton and zooplankton, respectively, and smelt were common. The second panel represents the period from ∼1982–1986 when flow was high, and NH_4^+ was increasing. During this period, the food web began to change. Under very low flow conditions, depicted by the third panel and representing ∼1987–1995, the NH_4^+ load was high, but PO_4^{3-} began to decrease. The food web also began to change significantly, with changes in the dominant phytoplankton and zooplankton, increasing abundance of macrophytes, increased importance of sediment nutrient processes, and increase in piscivores. Finally, post-1995, NH_4^+ loads remain high, while PO_4^{3-} loads are proportionately low. Sediment biogeochemical processes are of increasing importance in nutrient processing, macrophyte production is important, and omnivorous fish have increased. At the microbial level, *Microcystis* is more common and the zooplankton is dominated by cyclopoids, e.g., *Limnoithona* (color figure available online).

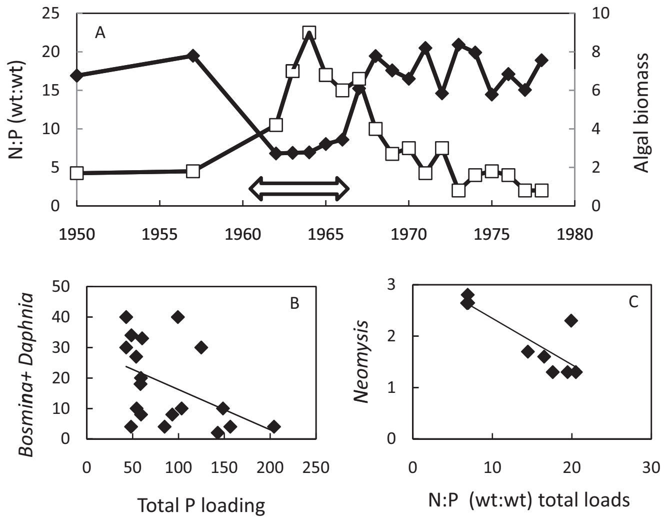

Figure 34 Comparative nutrient and food web relationships for Lake Washington: (A) change in N:P ratio (□; wt:wt) and change in algal biomass (◆; chlorophyll *a*, μg L^{-1}) as a function of time, (B) relationship between the abundance of *Daphnia* and *Bosmina* (number L^{-1}) and TP loading (10^3 kg yr^{-1}), and (C) relationship between *Neomysis* abundance (relative abundance) and the N:P ratio of the total nutrient load. Data were compiled from Edmondson and Lehman (1981), Edmondson and Litt (1982), Krebs (2008), and Eggers et al. (1978).

loading from a major sewage treatment plant compared to the more diffuse nutrient sources that affect the broader Chesapeake Bay. This river has been heavily impacted by nutrient inputs for over a century, with cyanobacterial blooms evident by the 1930s (Krogmann et al., 1986). Nutrient inputs to the Potomac have been strongly affected by management actions (Table 7), starting with treatment that removed 75% of point-source P loading by 1976 and with a P detergent ban, so that there was a total decrease of more than 95% from peak P levels (Jaworski and Romano, 1999). Nitrification was added to the treatment plant processing in the early to mid-1980s, resulting in decreased NH_4^+ loading; from the early 1990s to the present, effluent loads of NH_4^+ decreased more than 50% (Jaworski and Romano, 1999; Jaworski et al., 2007).

When N:P ratios increased in the late 1970s, chlorophyll *a* declined and SAV increased. Hydrilla, also an invasive species for this river, expanded its range shortly after P removal, and this correlated with a decrease in water-column chlorophyll *a* (Rybicki and Landwehr, 2007; Ruhl and Rybicki, 2010; Figure 35B). The extent of hydrilla coverage was directly related to the N:P ratios of the effluent (Figure 35C). After the nitrification–denitrification system had been installed at that treatment plant several years later, the relative abundance of this exotic species declined, while the abundance of native grasses and vegetation increased (Ruhl and Rybicki, 2010).

An invasion by *Corbicula fluminea* was first noted in the mid-1970s in the Potomac River. Its abundance peaked in the late 1980s, exceeding 2,500 individuals m^{-2} (Dresler and Cory, 1980; Phelps, 1994). Its peak occurred when the N:P of all loads was increasing. Its abundance subsequently declined, coincident with efforts to remove N from effluent and a decline in N:P (Phelps, 1994; Cummins et al., 2010; Figure 35A). Its presence in the 1980s was associated with declines in phytoplankton abundance due to the grazing pressure it imposed (Cohen et al., 1984). *Microcystis*, which had been a major component of the phytoplankton assemblage in the 1960s, declined in abundance with the installation of more advanced sewage treatment in the 1970s. However, over time, *Microcystis* returned. The percent of samples collected over time, in which $> 10\%$ of the phytoplankton cells were *Microcystis*, was also highly correlated with the N:P ratio in the total load of nutrients to the river (Tango et al., unpublished data; Figure 35D).

Fish composition also changed over time, and some of these changes can be related to nutrient stoichiometry. Bay anchovies decreased, and both spottail shiners and largemouth bass increased (http://www.dnr.state.md.us/fisheries/juvindex/

Table 7 Time line of changes in the Potomac River sub-estuary; most wastewater is discharged from the Blue Plains Facility

Years	Environmental change	References
1900–1970	P discharges from WWTP increase, peaking at $\sim 4.0 \cdot 10^6$ kg y^{-1} (100 kg m^{-2} y^{-1}); dissolved oxygen reaches minima ~1940	Jaworski and Romano (1999)
Late 1970s	With tertiary treatment and a P detergent ban, WWTP discharges of P decrease to $1.0 \cdot 10^6$ kg y^{-1} by 1976;	Jaworski and Romano (1999)
	Corbicula fluminea invades river, with variable but often high abundance until the early 1990s	Phelps (1994)
Early-to-mid 1980s	Nitrification added to WWTP leads NO_3^- discharge rather than NH_4^+; large upswing in surface water dissolved oxygen	Jaworski et al. (2007); Ruhl and Rybicki (2010)
1983–1991	Secondary drop in WWTP discharge of P to $<0.1 \cdot 10^6$ kg by 1986;	Jaworski and Romano (1999);
	SAV resurgence in the Potomac occurs, peaking with ~2000 ha of coverage dominated by *Hydrilla verticillata*	Rybicki and Landwehr (2007)
1984–1986	Fish surveys suggest doubling of large- and smallmouth bass with increasing SAV	US EPA (1993)
1986–present	SAV coverage decreases below peak levels, with low coverage in the mid-1990s and a resurgence in the early 2000s	Orth et al. (2010)
Early 1990s	N loading from WWTP peaks at $> 1 \cdot 10^7$ kg y^{-1}	Jaworski and Romano (1999);
Mid-1990s to present	N loading from WWTP decreases about 50% due to nitrification/denitrification process	Jaworski et al. 2007
	Corbula fluminea abundances decline significantly	
	Construction initiated at WWTP to reduce N loading by another 50% by 2014	Cummins et al. (2010)

index.asp#Indices) in proportion to N:P ratios that reflected changes in either total nutrient loads or effluent (Figures 35E,F). Overall, the ratio of pelagic:demersal fish declined (Kemp et al., 2005; www.noaa.chesapeakebay.net), and these changes related to the N:P ratio in the effluent (Jaworski et al., 2007; Figure 35G).

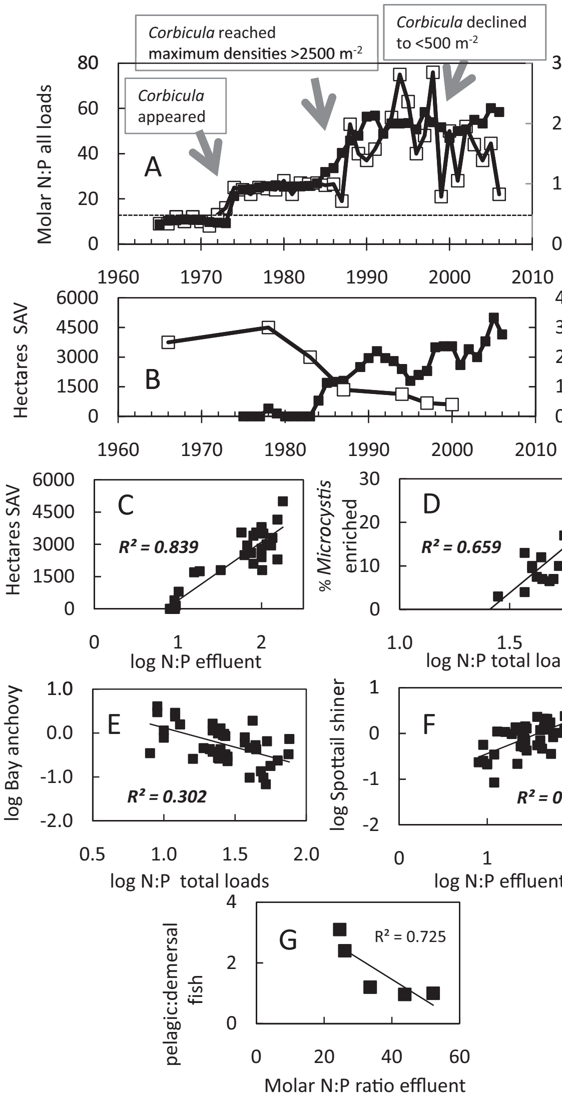

Figure 35 Comparative nutrient and food web relationships for the Potomac River. (A) Change in N:P ratio of all loads (■) and of the wastewater effluent only (□) as a function of time from the mid-1960s to 2005. Indicated also on the time course is the first appearance of the invasive *Corbicula fluminea* clams, as well as its maximum abundance and the time when they began to decline. Data were derived from Dresler and Cory (1980), Jaworski et al. (2007), and Cummins et al. (2010). (B) Change in abundance of SAV, in this case dominated by *Hydrilla* (■), and the change in chlorophyll *a* in the water column (□). Data were derived from Jaworski et al. (2007). (C) Relationship between the abundance of SAV (dominated by *Hydrilla*) and the N:P in the wastewater effluent. Data derived from Jaworski et al. (2007). (D) Relationship between the frequency of occurrence of water column samples enriched with > 10% *Microcystis* (by cell count) and the N:P in the total nutrient load. *Microcystis* data are courtesy of P. Tango from Maryland Department of Natural Resources monitoring program data (unpublished data); nutrient data are from Jaworski et al. (2007). (E) Abundance of Bay anchovy (log relative abundance as geometric mean catch per haul) as a function of N:P of the total nutrient load. (F) Abundance of spottail shiner (log relative abundance as geometric mean catch per haul) as a function of N:P in the effluent. Fish data from panels E and F are from Maryland Department of Natural Resources, Fisheries Service (http://www.dnr.state.md.us/fisheries/) and nutrient data are from Jaworski et al. (2007). (G) Ratio of pelagic:demersal fish as a function of the N:P ratio in the effluent. Fish data are from Kemp et al. (2005) and www.noaa.chesapeakebay.net, and nutrient data are from Jaworski et al. (2007).

Hudson River

Point source nutrient loading to the Hudson has been contentious for many decades (Brosnan et al., 2006). Secondary treatment plants were constructed in the 1980s, and N loads decreased by ~30%. Compared to the 1970s, reductions in P by ~60% were achieved by the 1990s through secondary treatment and P removal from detergents. The ratio of N:P loads from all sources to the Hudson also increased from the early 1970s to the mid-1990s (Howarth et al., 2006). The exception to these nutrient trends is the lower Hudson, where loads of both N and P *increased* due to the Ocean Dumping Ban Act of 1988, which required several municipalities to cease ocean disposal, and from New York City's use of a P-based buffer to reduce pipe corrosion (O'Shea and Brosnan, 2000; Brosnan et al., 2006). The TN and TP loads to the Hudson are now about 43 × 10^3 tonnes N yr^{-1} and 4.8 × 10^3 tonnes P yr^{-1}, of which 53% of the N and 77% of the P are from point source discharges (Howarth et al., 2006).

The Hudson, like the Bay Delta, has been heavily impacted by invasive species. Zebra mussels were first detected in the Hudson in 1991 and were well established by 1992 when P reductions had been implemented (Strayer, 2006). Their impact on the chlorophyll *a* and zooplankton populations of the river was large, and planktivorous fish soon became food limited (Caraco et al., 1997; Pace et al., 1998; Strayer, 2006). Average May–October chlorophyll *a* dropped from ~20 to ~4 μg L^{-1} after 1993 (Cole and Caraco, 2006). Like the Bay Delta, the common copepods in the Hudson now include two cyclopoids, in this case *Diacyclops bicuspidatus thomasi* and *Halicyclops* sp. (Pace and Lonsdale, 2006). The small estuarine invasive clam *Rangia* was first detected in 1988 and has spread significantly since that time (Strayer, 2006).

Increases in largemouth bass and bluegills have been observed since nutrients have changed, and, analogous to the Bay Delta, the length of American shad has decreased since P removal and zebra mussel invasion (Stanne et al., 2007). There have also been large increases in water chestnut (*Eleocharis dulcis*), an aggressive macrophyte that was first observed in the Hudson in the 1930s. It has especially increased during recent decades, with "larger beds reaching 10–100 hectares in extent" (Strayer, 2006, p. 302). In these dense beds, oxygen depletion occurs (Caraco and Cole, 2002). *Microcystis* is now a concern in the Hudson River as well (Fernald et al., 2007). It had been problematic years earlier, but disappeared from the river soon after zebra mussels invaded (Smith et al., 1998). Laboratory studies indicated that it was preferentially grazed by the mussels (Baker et al., 1998; Baker and Levinton, 2003). However, these blooms have returned; by 2005, *Microcystis* contributed more than 45% of the total summer algal biomass (Fernald et al., 2007). Recent reports have linked these blooms to increased temperature (e.g., Fernald et al., 2007), but the pattern is also consistent with an altered biogeochemical pathway of nutrient cycling following the increased dominance of both macrophytes and zebra mussels. Temperature may be a necessary condition, but it is not a sufficient explanation of changes in this species over time.

European Lakes and Estuaries

In the Ebro River Estuary, where an 18-year time series of nutrients and biota has been examined, significant changes in the food web have occurred as nutrient loadings have changed. From the mid-1980s to the mid-1990s, P loading rates were consistently high, and NH_4^+ loading increased. Both decreased precipitously in the mid-1990s (Ibáñez et al., 2008). For P, this drop was from $\sim$2.8 kt y^{-1} to $<$0.5 tonnes y^{-1}. However, TN load did not decrease to the same extent because $NO_3^-+NO_2^-$ loads were not reduced. Consequently, mean values of DIN:DIP increased over four-fold from the early 1990s to the mid-2000s. Total water-column chlorophyll *a* declined by $\sim$ten-fold, macrophyte production increased, sediment retention and transparency increased, and invasive bivalves increased, including *Dreissena polymorpha* and *Corbicula fluminea* (Ibáñez et al., 2008). These changes were attributed to the reduction in P loads (Ibáñez et al., 2008). In the Dutch Delta, Lake Veere provides another example of system change upon PO_4^{3-} removal; when PO_4^{3-} was reduced, following the restoration of exchange with the tidal marine eastern Scheldt, there was an increase in bivalves among other ecosystem changes (Wijnhoven et al., 2010).

In another example of the relationship between P reduction and zebra mussels, a study of the recovery of eutrophication in Lake Velume, The Netherlands, showed that zebra mussels expanded following P reduction (Ibelings et al., 2007). The zebra mussels in turn, like the macrophytes, further structured the food web, including fish. Lakes in southern Sweden have shown similar patterns; Lake Krankesjön shifted to a clear state when P was reduced, with a concomitant expansion of pondweed and piscivorous fish, while Lake Tåkern sustained a reduction in submersed vegetation and an increase in phytoplankton chlorophyll *a* when nutrients, especially P, increased (Blindow et al., 2006; Hargeby et al., 2007). Zebra mussels were also highly associated with *Microcystis* abundance in 47 sites in lakes in northern Ireland, and all of these lakes had toxic blooms (Mooney et al., 2010).

Summary of Part IV

The Bay Delta data and the other systems considered here which are undergoing similar changes in nutrient stoichiometry have had a similar general trajectory of responses (Table 8). While all of the systems described above have undergone complex changes, largely a result of direct management actions, there are many parallels with respect to organism dominance after P removal. While invading species such as hydrilla and *Egeria*, and many bivalve molluscs do well across a range of system types, the commonality of the increased frequency of invasion around the time P was removed throughout much of the United States and Europe raises interesting questions about cause-and-effect related to altered nutrient stoichiometry. Moreover, the physiology of the resident organisms and biogeochemical pathways lend support to the premise that similar

Table 8 Descriptive comparison of major food web changes in comparative systems after reduction of P from the system and the associated increase in the disolved N:P ratio; further details of all of these changes are described more fully in the text

	San Francisco Estuary	Lake Washington	Potomac River	Hudson River	Ebro River
Phytoplankton					
Change in Chl:*a*	Decrease	Decrease	Decrease	Decrease	Decrease
Change in *Microcystis* occurrence	Increase	Decrease	Initial decrease, then resurgence	Initial decrease, then resurgence	
Zooplankton					
Change in species group	Increase in cyclopoids and cladocerans Decrease in *Neomysis*	Increase in cyclopoids and cladocerans Decrease in *Neomysis*	Increase in cyclopoids and cladocerans	Increase in cyclopoids and cladocerans	
Fish					
Change in dominant feeding strategy	Decrease in planktivores: piscivores		Decrease in planktivores: detritivores	Decrease in planktivores	
Bivalves					
Change in dominant species	Increase in *Corbula*		Increase in *Corbicula*, *Rangia*	Increase in *Dreissena*, *Rangia*	Increase in *Dreissena*, *Corbicula*
Submersed vegetation					
Change in abundance	Increase		Increase	Increase	Increase
Dominant species	*Egeria, Eichornia*		*Hydrilla*	*Hydrilla, Eleocharis*	*Hydrilla*

Blank entries are those for which insufficient data are available to evaluate.

trophic structure, including the appearance of *Microcystis*, in many of these systems has resulted from similar nutrient dynamics. Biogeochemistry, and food web interactions that both modify and result from changes in stoichiometry and the relative abilities of different types of organisms to either sequester nutrients and/or to tolerate nutrients that are in excess (e.g., NH_4^+).

PART V: ECOLOGICAL STOICHIOMETRY AND PREVAILING VIEWPOINTS

The interpretation of changes in the food web structure of the Bay Delta as a function of stoichiometric changes in nutrients seems at odds with prevailing perspectives of how this system has become stressed over time. Nixon and Buckley (2002), in a general review of the relationships between nutrient loadings and fish production, discussed the evolution of the concept of linking nutrients to fish and tracked how this concept generally fell out of favor. Among the reasons cited was the recognition that "the last 100 years of marine research revealed a much richer and more complex marine environment than anyone working in the 1900 could have imagined, ultimately leading to the conclusion by Micheli (1999) that there is "…virtually no link between nutrient delivery or availability and secondary production in marine coastal waters" (Nixon and Buckley, 2002, p. 784). This "rich complexity" of effects has led to a range of interpretations about changes in the food web in the Bay Delta, most of which have not involved nutrient control.

With respect to the Bay Delta ecosystem, the possibility of bottom-up control of fish populations in the Bay Delta has been largely dismissed for several reasons: most nutrients are at levels that saturate phytoplankton growth; phytoplankton growth is considered to be regulated primarily by light limitation (Cole and Cloern, 1984); NH_4^+ is generally a preferred form of N for phytoplankton uptake (McCarthy et al. 1977; Millero, 2006; Jassby, 2008); the pH of the receiving waters is generally in the range that prevents formation of toxic NH_3 (Jassby, 2008); and NH_4^+ levels are typically below the criteria considered by the U.S. Environmental Protection Agency (2009) to be toxic to sensitive aquatic life, such as freshwater molluscs. In addition, some analyses of nutrient effects have considered only TN or TP and chlorophyll *a*, rather than nutrient form and phytoplankton composition (e.g., Jassby, 2008). As a consequence, relationships between nutrients, production, or food web effects have been obscured or ambiguous (Jassby, 2008). Moreover, because many physical, chemical, and biological factors potentially influence and modify other factors, the system as a whole is considered highly complex, and this conclusion has been underscored by several prior efforts (Bennett and Moyle, 1996; Sommer et al., 2007; Mac Nally et al., 2010; Thompson et al., 2010).

Prevailing views about changes in the Bay Delta food web emphasize invasive species, light limitation of primary production, food limitation, alteration in flows (including export pumping), alterations in habitat, and climate change (both temperature and hydrologic changes) as major stressors (Linville et al., 2002; Davis et al., 2003; Lehman, 2004; Lehman et al., 2005; Bennett, 2005; Sommer et al., 2007; Jassby, 2008; Baxter et al., 2010; Winder et al., 2011). The effects of climate are recognized to act synergistically with many stressors in the Bay Delta and elsewhere (e.g., Lehman, 2000; Burkholder et al., 2006, Paerl et al., 2006; Cloern et al., 2007; Paerl and Scott, 2010, Winder et al., 2011). Where nutrients have been considered to be important in the food web changes over the past decades, the emphasis has been on understanding the potential inhibition of primary production and the decline in diatoms associated with elevated levels of NH_4^+ (e.g., Wilkerson et al., 2006; Dugdale et al., 2007) rather than on nutrient limition or nutrient stoichiometry. Both the prevailing and the stoichiometric viewpoints underscore that the system is stressed and complex. The prevailing views related to limiting factors, nutrients, flow, and habitat alteration are examined below in comparison to stoichiometric interpretations.

Light Limitation of Primary Producers

Dissolved nutrients generally have been perceived to play, at most, a minor role in controlling the succession of biota in the Bay Delta over the last 30 years, and primary production is considered to be mainly controlled by light. These generalizations stem from modeling studies of phytoplankton productivity as applied to the San Francisco Estuary (Cloern et al., 1995; Cloern, 1999; Jassby et al., 2002). The results of the models indicated that over much of the estuary, particularly the upper estuary, ambient nutrient concentrations over the last ~30 years generally were well in excess of the demand for those nutrients, given the available light in the water column to drive photosynthesis; i.e., the phytoplankton were strongly light-limited and not nutrient-limited for growth. Models were developed (Cloern et al., 1995; Cloern 1999) to simulate phytoplankton primary productivity in the San Francisco Bay Estuary based on the availability of resources (light and nutrients) in the system and empirical "physiological" relationships. The influence of nutrients was formulated using assumptions of uptake kinetics with respect to ambient concentrations and an interactive term with light harvesting to account for photoacclimative changes in chlorophyll *a*:C (Chl:C) ratios under different nutrient stress levels. The models were parameterized using mean relationships from large datasets (Cloern, 1999). Importantly, however, the wide plasticity in nutrient uptake kinetics among species and within species under varying growth conditions was not considered (e.g., Rhee, 1973; Burmaster and Chisholm, 1979; Gotham and Rhee, 1981; Goldman and Glibert, 1982, 1983; Morel, 1987). A subsequent model developed by Jassby et al. (2002), which did not include a nutrient term, exhibited good fidelity with independent productivity measurements, suggesting to the authors that primary productivity was independent of nutrients in the system. Therefore, the models were taken as substantially accurate in the context of distinguishing light from nutrient limitation of C production by the phytoplankton.

The fundamental assumption in these models is that *primary production* is the principal factor that links phytoplankton to the grazer community and upper trophic levels. This conventional approach for determining the amount of energy (as reduced C) that would be available to upper trophic levels unfortunately ignores the transfer of elements other than C. In marked contrast and as developed herein, ecological stoichiometry dictates that it is the processing and transfer of all elements, especially N and P, through the phytoplankton assemblage that drives the fitness of species at higher trophic levels (Sterner and Elser, 2002; Allen and Gillooly, 2009; Schoo et al., 2010; Malzahn et al., 2010). No insight into these aspects of community response can be drawn from the existing C-based primary production models. As illustrated in the analyses above, nutrients that are at levels normally taken to be saturating or near-saturating can influence the elemental composition of the phytoplankton (food quality) and, therefore, differentially affect the transfer of N and P to upper trophic levels via trophic transfer and via altered biogeochemical dynamics.

Potential Inhibition of Diatoms by NH_4^+

The effect of NH_4^+ on diatom production has received considerable recent attention in the Bay Delta (e.g., Wilkerson et al., 2006; Dugdale et al., 2007; Van Nieuwenhuyse, 2007; Jassby, 2008; Glibert, 2010). Many algae, especially those that are N-limited, prefer NH_4^+ as an N source because it is already in reduced form and thus more easily assimilated (Harris, 1986; McCarthy et al., 1995, 1977). However, some diatoms physiologically prefer, and in some cases require, nitrate ($NO_3{}^-$) over NH_4^+ (Lomas and Glibert, 1999). This phenomenon is accentuated when the cells are in a state of energy imbalance, such as might be experienced under varying light regimes; for these cells, $NO_3{}^-$ may also be used in maintaining the cellular energy balance in addition to providing a nutrient (Lomas and Glibert, 1999). In San Francisco Bay, Wilkerson et al. (2006) and Dugdale et al. (2007), based on enclosure experiments, reported that diatoms grew only after NH_4^+ concentrations were drawn down to $<4\ \mu$M (0.056 mg L^{-1}).

An interesting "natural test" of the potential inhibition of diatoms by NH_4^+ occurred during summer 2010, when such inhibition was "relaxed" because discharge of NH_4^+ from the SRWWTP was ∼15% lower than in the immediate prior years (R. Dugdale, personal communication). The decreased NH_4^+ loads coincided with a spring diatom bloom that was observed in Suisun Bay for the first time in many years. Moreover, consistent with the trophic interactions seen in the long-term data, in spring 2010, *Eurytemora* density was 3.1-fold higher than in 2009, and increases were also noted in *Pseudodiaptomus* density and in the 2010 FMWT index of delta smelt abundance.

Food Limitation

Food limitation has been invoked by numerous researchers as key to the decline in the Bay Delta food web over time (Bennett and Moyle, 1996; Jassby et al., 2002, 2003). Total productivity has been estimated to be comparatively low relative to other estuaries, and detritus appears to be an important food supplement for grazers (e.g., Müller-Solger et al., 2002). However, from a stoichiometric perspective, detritus, which is high in C, may result in metabolic costs to consumers, including altered metabolic rate and growth rate (Plath and Boersma, 2001; Hessen and Andersen, 2008). Detritivores consume the least nutritionally balanced foods and, thus, have lower growth rates than their planktivorous or piscivorous counterparts (Sterner and Elser, 2002). In keeping with this notion for the Bay Delta, Sobczak et al. (2005) found that while detritus may support a significant fraction of the heterotrophic metabolism of the system, it did not seem to support pelagic food webs, leading to higher trophic levels. Disposal of excess C appears to have major impacts on organismal fitness and, like the other stoichiometric concepts explained above, can affect ecological interactions at the ecosystem level (Hessen and Andersen, 2008).

Variations in Flow and Habitat Suitability

Of considerable interest to resource managers in the Bay Delta are the effects of hydrologic changes on pelagic fish (e.g., Nichols et al., 1986; Jassby et al., 1995; Kimmerer, 2002; Moyle et al., 2010). The question of relationships between hydrology and biodiversity are also of importance in many systems (e.g., Ferreira et al., 2005). In the Bay Delta, flow is rigorously managed and measured by the location where salinity is equal to 2, measured as the distance from the Golden Gate Bridge ("X2"; Jassby et al., 1995; Kimmerer, 2004). X2 is therefore considered to be a proxy for outflow.

Strong bi-variate, correlative relationships have been reported between X2 and chlorophyll *a*, *Eurytemora, Acartia*, rotifers, mysids, clams bay shrimp, and various fish species, including longfin smelt, splittail, and starry flounder (Kimmerer, 2002; Winder et al., 2011). Interestingly, many of these relationships were noted to change after 1987 (Kimmerer, 2002). This has been thought to be due to the drought that began in the 1980s and which may have changed habitat suitability, especially allowing more invasive organisms (Winder et al., 2011). The change after 1987 also corresponds with the change in nutrient loading. X2 is strongly correlated with PO_4^{3-}, TP, and NH_4^+ (Figure 36). For comparison with nutrient relationships, the relationships between the parameters studied here and X2 have been calculated using the same approaches (Table 9). For all organisms (with the exception of *Acartia*, for which strong correlations were observed with X2-Table 9), i.e., *Eurytemora*, *Pseudodiaptomus*, *Daphnia*, *Bosmina*, *Corbula*, *Crangon*, longfin smelt, splittail, striped bass, starry founder, crappie, sunfish, and largemouth bass, equal or more significant correlations were

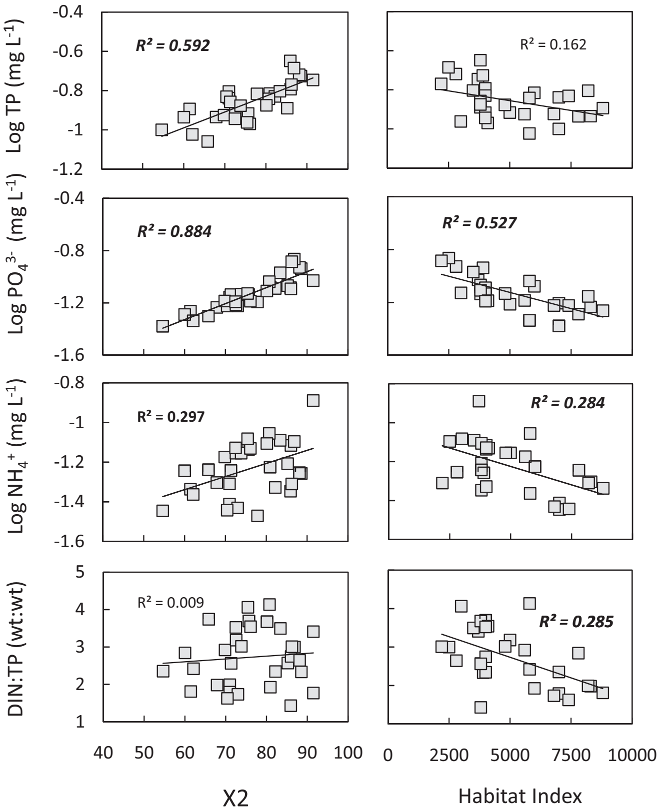

Figure 36 Comparison of the relationships between TP, PO_4^{3-}, NH_4^+, and the DIN:TP ratio versus X2 (the isohaline where salinity = 2, measured as distance (km) from the Golden Gate Bridge) and versus the habitat index (defined by salinity, temperature, and turbidity relationships; Feyrer et al., 2010) for the time course from 1975–2005. Coefficients of determination (R^2) are given for the entire dataset. Those indicated in bold are significant at $p < 0.05$, those in bold italics are significant at $p < 0.01$. The analysis indicates significant relationships between X2 and TP, PO_4^{3-}, and NH_4^+ concentrations and significant relationships between the habitat index and $PO_4{}^{3-}$, NH_4^+, and the DIN:TP ratio.

observed with nutrients or nutrient ratios (Tables 4 and 5). That strong relationships between some organism changes and X2 are found is without question; however, the strong relationships between nutrients and X2 leads to uncertainty as to whether salinity (or flow) or nutrients are the controlling variables. Furthermore, when calculated as pre-whitened or differenced data, versus the original or smoothed data, more correlations were significant, suggesting that higher frequency time scale changes may be a component of this variability (Pyper and Peterman, 1998). This contrasts with the nutrient relationships, for which many relationships were stronger in the original or smoothed data, suggesting that longer-term variability (i.e., unidirectional trends) is important.

A relationship has also been developed between X2 and a habitat index for delta smelt, an index that uses salinity, turbidity, and temperature to define the spatial distribution of habitat suitability. This index explained 26% of the variability in delta smelt over the past three decades (Feyrer et al., 2010). This habitat index, like X2, is highly correlated with nutrients (Figure 36). As shown here, TP explained at least as much of the variability in delta smelt as did the habitat index (Table 4), and dinoflagellate abundance explained even more (Table 6).

Moyle et al. (2010) suggested that variability and disturbance are required to re-establish native fish populations. They argued that the changes over time in fish populations are the result of "an altered physical environment in which the Delta has become simplified into a channelized conveyance system to support export of fresh water from and through the Estuary during summer and to reduce freshwater outflows at other times of year. Suisun Bay and Suisun Marsh have become essentially a brackish water system, while San Francisco Bay has become more consistently a marine system, as shown by fish distributions" (Moyle et al., 2010). This notion is based on the premise that when disturbance is low, the system moves to a new equilibrium, where those species whose competitive abilities are low may be lost (Moyle et al., 2010, citing Krebs, 2008). Interestingly, in aquatic systems, homeostasis tends to dampen the effects of physical disturbance (Krebs, 2008). Moyle et al. (2010) did acknowledge that water quality is important in multiple ways, that their analysis is highly speculative, that freshwater brings many of the nutrients required to fertilize the food web, and that excessive nutrients (including effluent) from large treatment plants need to be addressed.

Summary of Part V

The response of the system to nutrients sets in motion a cascade of interacting effects. Thus, to varying degrees, nutrients, flow, X2, invasive species, and warming or hydrologic changes are all related to the observed changes in the food web (e.g., Kimmerer, 2002; Winder et al., 2011), and it is not surprising that some of these relationships are statistically significant. Yet, all of these relationships can also be explained by a stoichiometric model. Using stoichiometry, the trajectory of responses to changing nutrients over time provides a new interpretation for the decline in pelagic fish species in recent years, the POD. The current conceptual understanding is based on a "multi-stressor hypothesis" that relates a complex interplay of stressors, ranging from predation and water exports (top-down control), to prior abundance levels (life history and density-dependent effects), to changes in the physical and chemical environment, to changes in food availability and quality, that combine to form an overall stress on certain populations (Sommer et al., 2007; Baxter et al., 2010). In contrast, the stoichiometric interpretation argues that many of these factors and changes are linked and may be sequential, with nutrient changes being a major driver (Figure 37). Nutrient changes, and the biochemical changes that follow as a consequence, alter the environment, potentially making it more conducive to invasive species, and differential nutrient metabolism and homeostasis drives the system away from planktivores to omnivores or piscivores as N:P changes.

Table 9 Correlation coefficients (r) for various organisms shown and X2

	X2 (km)			
	Original data	Pre-whitened	First-differenced	Three-year moving average
Organism				
Phytoplankton				
Chlorophyll a (μg L^{-1})		−0.70**		
Bacillariophyceae (cells mL^{-1})		−0.58**	−0.58**	
Chlorophyceae (cells mL^{-1})				0.45*
Cryptophyceae (cells mL^{-1})				
Dinophyceae (cells mL^{-1})			0.37	
Cyanobacteria (cells mL^{-1})				
Zooplankton				
Eurytemora (individual m^{-3})		−0.52**	−0.43*	
Sinocalanus (individual m^{-3})	−0.56**			−0.69**
Acartia (individual m^{-3})	0.57**	0.57**	0.62**	0.40*
Pseudodiaptomus (individual m^{-3})		−0.58**	−0.81**	
Harpacticoids (individual m^{-3})				
Limnoithona (individual m^{-3})	−0.38	−0.59**		−0.49
Daphnia (individual m^{-3})	−0.76**	−0.75**	−0.79**	−0.79**
Bosmina (individual m^{-3})	−0.87**	−0.85**	−0.50**	−0.87**
Neomysis (individual m^{-3})			−0.49**	
Invertebrates				
Corbula (count/grab)		0.70**	0.57*	
All crabs (individual m^{-2})	0.41	0.58**		
Crangon (individual m^{-3})		−0.52**	−0.48**	
Palaemon (individual m^{-3})				
Fish				
Delta smelt (STN index)				
Delta smelt (FMWT index)			−0.35	
Longfin smelt (FMWT index)	−0.71**	−0.80**		−0.67**
Splittail (FMWT index)	−0.57**	−0.55**	−0.47*	−0.65**
Threadfin shad (FMWT index)				−0.42*
Striped bass (FMWT index)		−0.34*	−0.46*	
Yellowfin goby (FMWT catch per tow)			−0.51**	
Starry flounder (FMWT catch per tow)	−0.36*	−0.41*		−0.42*
Crappie (relative abundance)	−0.60**	−0.66**		−0.79**
Sunfish (relative abundance)	−0.47**	−0.58**	−0.36*	−0.51*
Largemouth bass (relative abundance)		−0.47*	−0.59**	−0.44*
Silversides (relative abundance)		0.38*		

All organism parameters were log-transformed. For each data series, the first column shows the correlations of the original data (log-transformed), the second column shows the correlations of the trend stationary data, the third column show the correlations of the difference stationary data, and the fourth column shows the correlations of the data transformed as three-year backward moving averages. The correlations are for the entire time series. Only values for $p < 0.10$ are shown; values that are significant at $p < 0.05$ are indicated by *, and those significant at $p < 0.01$ are indicated by **. Negative correlations are highlighted in blue, and positive correlations are highlighted in pink ($p < 0.05$ [lighter shade] and 0.01 [darker shade] only).

PART VI: CONCLUSIONS, IMPLICATIONS AND RECOMMENDATIONS

Conclusions

Eutrophication, ecological stoichiometry, and alternate stable state theories can be combined to form unifying framework for understanding the complexity of responses, not only in the Bay Delta but also, more generally, in many comparative systems. This interpretation does not negate the importance of ecological invasions, habitat changes, multiple stressors, and food web complexities, but it adds a *mechanism* to those interpretations through biogeochemistry and organismal stoichiometry. Ecological stoichiometry affects systems by setting elemental constraints on the growth of organisms. This, in turn, affects food quality and the relationships between predators and prey. The biota modify the environment through nutrient regeneration, which differs from species to species based on their elemental requirements and nutrient sources. Growth also modifies the physical and chemical environment through pH changes, habitat alteration, light environment, and substrate, among other factors. An overarching driver is the importance of bottom-up control. Top-down control can be considered as a secondary effect, that is, a consequence of altered nutrients; the composition of the grazers changes in relation to stoichiometric constraints. In the Bay Delta, evidence is clear that top-down grazing of phytoplankton by *Corbula* exerts a strong control on phytoplankton biomass, as is also the case for other systems, such as the Potomac and the Hudson, when invaded by bivalve molluscs. However, the arguments presented here make the case that bottom-up control contributed to the all-important conditions that allowed *Corbula* to become a dominant regulator of phytoplankton production. Winder et al. (2011) suggested that such a niche for *Corbula* opened up due to climate change and its effect on hydrology. Prior interpretations, emphasizing stochastic invasions largely via ballast water exchange, imply that the invasive event was the ultimate cause of the change in top-down control of phytoplankton. The ecological stoichiometric interpretation does not preclude strong top-down control of selected component organisms, nor ballast water exchange as the mechanism of introduction. The distinction is that, at the overall ecosystem level, the structuring of species is affected by alterations in nutrients and ecosystem biogeochemistry. This interpretation is consistent with Ware and Thompson's (2005) insights from a broad survey of the relative contributions of bottom-up versus top-down factors that potentially control fish catch in the coastal waters of the western United States; they, too, reported that bottom-up factors were more important.

The similarity in responses of the comparative systems described here supports the need for a new phase of understanding of nutrient loading impacts. In Cloern's (2001) Phase III model of eutrophication, interactions of multiple stressors and nutrients resulted in complex interactions and changes in plankton and benthic communities (Figure 2). Described here are several common responses of complex aquatic ecosystems to increased or sustained N loading and concomitant P reductions (Figure 38). These commonalities, including reduced levels of chlorophyll *a*, increased SAV (particularly rooted macrophyte) growth, and a shift in dominance to large omnivorous/piscivorous fish, have been, in some cases, interpreted as oligotrophication (e.g., Anderson et al., 2005; Collos et al., 2009). However, an additional feature that these ecosystems have in common is susceptibility to invasive species, particularly bivalve molluscs. Systems in which either N or P, but not both, are controlled are in a unique trophic state, neither eutrophic nor oligotrophic; they have been forced into a state of *stoichiotrophic change* or *imbalance*. Specific trophic responses, based on stoichiometric constraints, can be predicted for stoichiotrophically imbalanced systems. Moreover, stoichiometric regulation can be important for food web dynamics, even when changes in these nutrients and their ratios are not widely divergent from Redfield proportions – that is, whether N or P are limiting, or not.

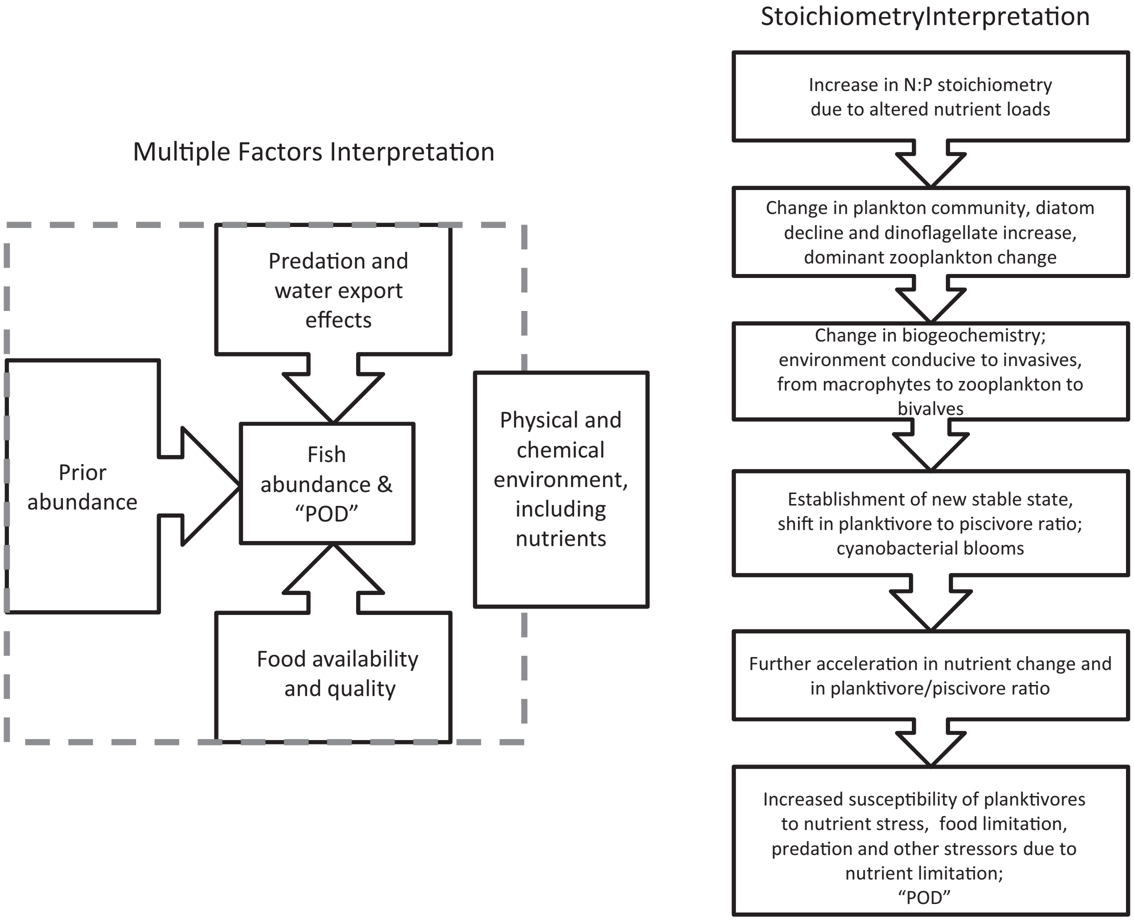

Figure 37 Comparison between the conceptual understanding of the factors related to the Pelagic Organic Decline (POD) as described by Sommer et al. (2007) and the conceptual understanding described in this analysis.

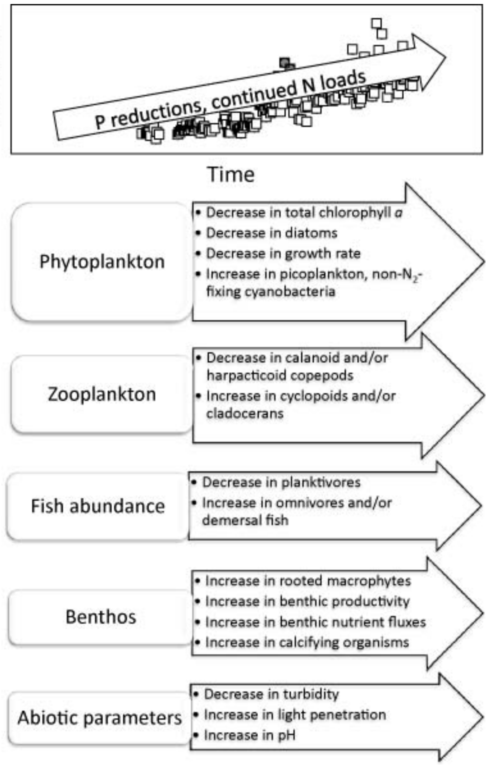

Figure 38 Generalized trajectory of responses for systems impacted by imbalances in N:P stoichiometry where P loads have been reduced and N loads have been increasing.

The trajectory of ecosystem responses in the Bay Delta, illustrated here, suggests that as nutrient stoichiometry changed over time and the system shifted from high flow to low flow back to high flow, it did not return to the same condition (e.g., Figure 33). The likely reason for this failure to return to its historic condition is the reservoir of P in sediments and the potential for this reservoir to be mobilized under varying flow conditions. Nutrient enrichment can destabilize the dynamics of consumers, the "paradox of enrichment" (Naddafi et al., 2009), and this appears to have occurred in the Bay Delta in a manner similar to other systems. Thus, while complex, the Bay Delta is not uniquely complex among estuaries or, indeed, among aquatic ecosystems, as suggested by Kimmerer (2004). When flow returned to high levels after the mid-1980s drought, bivalves and other organisms had become established, and the biogeochemistry of the system was altered relative to pre-drought conditions. A new stable state had emerged, setting in place the conditions that accelerated further ecosystem change. The new condition no longer provided the same relationships between fish abundance and flow as had the earlier condition; nutrient effects overwhelmed flow effects. Nutrients may thus provide a mechanism whereby "invasional meltdown" can be accelerated (Simberloff and Von Holle, 1999).

The analysis here extends that of Glibert (2010), who also examined both N:P ratios and NH_4^+ and their effects on the food web in the Bay Delta using cumulative sums of variability analyses (CUSUM; e.g., Page, 1954) applied to nutrient changes and major trophic components. As background, CUSUM-transformed relationships compare the accumulation of a quantity over time; CUSUM is, in effect, a low-pass filter for time series analysis. Correlations of CUSUM-transformed variables, or double-mass curve analysis (e.g., Kohler, 1949; Searcy and Hardison, 1960), allows the pattern of change in two variables to be compared, recognizing that such comparisons improve the signal-to-noise ratio and associated change points. In ecology, the application of single-mass (CUSUM) and double-mass analysis has been increasing, and the CUSUM approach has been identified as an important tool in regime change analysis (Andersen et al., 2008). Comparison of CUSUM curves allowed visualization of how long different components of the food web exhibited similar trends relative to their long-term means (Glibert, 2010).

Based on CUSUM analysis, Glibert (2010) conceptualized three different major food webs over time: a diatom-*Eurytemora*-delta smelt period prior to 1982, a mixed phytoplankton (cryptophytes-green algae-other flagellates)-*Pseudodiaptomus*-bass-shad period from 1982 to ∼2000, and a cyanobacteria-*Limnoithona*-silverside-largemouth bass-sunfish period post-2000. CUSUM comparative curves provide visually accentuated patterns, allowing interpretations of commonalities in the timing of shifts in variables. Both sets of analyses (this study and Glibert, 2010) showed strong correlations between changes in the food web and nutrients. Both also demonstrated changes in fish populations as a function of DIN:DIP and NH_4^+ and in relation to *Eurytemora* abundance, and both identified the *timing* of these changes. The stoichiometric and biogeochemical constraints presented in this review provide plausible mechanisms for why these food webs changed as they did. Comparisons across systems have provided evidence of commonalities in changes in food webs when nutrient stoichiometry is altered.

A central conclusion of this analysis is that *P control, without concomitant N control, has unintended consequences*. As seen for the Bay Delta here and in previous analyses (Van Nieuwenhuyse, 2007) and in the comparative systems described above, P reductions can result in a decline in chlorophyll *a*. Where cyanobacterial blooms previously had been problematic, they declined initially, as in the Potomac River. However, once benthic primary producers take hold, and their productivity increases, the sediment "pump" of stored P begins to provide this nutrient in sufficient quantities that organisms, such as dinoflagellates, or cyanobacteria, such as *Microcystis*, can become established or re-established. If the system also receives N in the form of NH_4^+, only organisms that can tolerate high concentrations of NH_4^+ are apparently able to thrive—including, for the Bay Delta, certain macrophytes, bivalves, cyanobacteria, cyclopoids, and omnivorous/piscivorous fish. Thus, it is the interplay of P sequestration and NH_4^+ tolerance that contributes to shifts to new dominants; this interplay is clearly illustrated in the strong positive or negative correlations of many species at all trophic levels with DIN:TP or DIN:DIP (Table 5).

Those organisms that can successfully sequester P will become dominant when P reductions are made, because the sediment will continue to provide this nutrient. Once the sediment P pump has become established, the system can be viewed as having reached a tipping point, wherein further P reductions likely will only exacerbate the problem. Key among these associations is the NH_4^+ sensitivity of diatoms, which are strongly associated with the success of many species (Table 6). Their decline has consequences for the food web at many levels.

Two management strategies are envisioned for systems undergoing ecosystem changes associated with stoichiotrophic imbalance: either increase the P load or decrease the N load. Increasing P—for systems that are rich in N—risks pushing the system toward a classical eutrophied condition, with concomitant increased hypoxia/anoxia and unfavorable changes in the benthic community. Reductions in N (especially NH_4^+) will allow organisms, from diatoms to fish, that cannot withstand high NH_4^+ (and/or that are outcompeted by NH_4^+-tolerant organisms, such as various harmful dinoflagellates and cyanobacteria) to compete. The challenge for resource managers is how to recognize when such a tipping point has occurred and when aggressive P reductions would therefore be counter-productive. This conclusion contradicts some authors, such as Carpenter (2008) and Schindler et al. (2008), who view P reductions as the sole solution to eutrophication, but supports that of Fisher et al. (1992), Hagy et al., (2004), Burkholder et al. (2006), Howarth and Paerl (2008), Conley et al. (2009), and Paerl (2009), who view both N and P controls to be necessary. Control of P works to a point but appears not to be able to overcome the biogeochemical "pumping" of P from P-laden sediments into the overlying water. Initial responses, such as chlorophyll *a* and bloom reductions in response to P control, may give resource managers a false sense of success; once the threshold of biogeochemical control has been crossed, more P control is not the solution. The same biogeochemical regulation of P release supporting cyanobacterial blooms in the Baltic Sea has been reported, where it has been strongly emphasized that "During longer time scales, reductions in external phosphorus load may reduce cyanobacterial blooms; however, on shorter time scales the internal phosphorus loading from the sediment can counteract external phosphorus reductions" (Vahtera et al., 2007, p. 1).

Interestingly, in 2010, additional P reduction measures, i.e., removal of P from dishwashing detergents, were taken in California. Stoichiometric and biogeochemical regulation would suggest that N control is much more imperative. New requirements for effluent removal from the major wastewater treatment plant (WWTP) on the Sacramento River call for reductions in N loading from the current 14 to 8 tonnes day^{-1} (2.2 mg L^{-1} NH_4^+ + 10 mg L^{-1} $NO_3{}^-$; permitted up to 181 mgd) in the coming decade through implementation of nitrification and denitrification (Central Valley Regional Water Quality Control Board, 2010). This biological nutrient removal would result in a significant decrease in effluent DIN:TP ratios. Riverine N:P is not expected to change to this extreme, however, due to other nutrient loading sources (Sobota et al., 2009). Inasmuch as P levels are approximately what they were in the early 1970s when the food web supported such fishes as abundant delta smelt, it is N that must be reduced, rather than P that should be increased, to achieve the desired balance and food web restoration.

In further support of N reduction, restoration efforts in the Potomac are showing evidence of reduction in exotic species and a return of native vegetation following the reduction in wastewater N (Ruhl and Rybicki, 2010). Similarly, a 57% reduction in N loading in Tampa Bay between the 1980s and 2002 led to extensive recovery of native seagrasses, and a similar recovery was observed for Sarasota Bay following a 46% reduction in its N loading (Johansson and Greening, 2000; Tomasko et al., 2005; Ralph et al., 2006). Elemental stoichiometry provides the theory, and the Potomac River and Tampa Bay provide examples, that the Bay Delta's food web will likely be altered favorably under the projected nutrient regime of the Bay Delta once N controls have been enacted.

Broader Implications

A number of broader implications emerge from this analysis.

(1) The patterns in invasions of species in the Bay Delta and the comparative systems described herein are generally supportive of the emerging concept that invasions are not strictly stochastic events; rather, environmental changes interact with vectors of invasion to enhance their success (e.g., Hobbs, 2000; Kolar and Lodge, 2001). There have been numerous other examples where ecosystem disturbance has been associated with the opportunity for species to colonize following new introductions and/or for latent populations to expand (Hobbs and Huenneke, 1992; Hobbs, 2000). That the pattern of trophic cascades is similar in systems ranging from the Bay Delta to the Potomac River and elsewhere is evidence of the similar paths that systems undergo in biogeochemistry and biological interactions when nutrients are altered. Changes in land use, nutrient loading, and climate-related changes have all been associated with successful species invasions (Carlton, 2000; Winder et al., 2011). To this list, the interacting effects of P reductions and static or increasing N loads are an important addition.

(2) There has been much debate about nutrient regulation and limitation, most recently in a set of papers about the potential importance of N versus P in estuaries (Schindler et al., 2008; Schindler and Hecky, 2008; Howarth and Paerl, 2008; Carpenter, 2008; Conley et al., 2009). Schindler argued that P is the limiting nutrient in lakes, and therefore, eutrophication can be controlled by controlling that nutrient. Others have argued for the need for control of both nutrients in estuarine and freshwater systems (e.g., Fisher et al., 1992; Paerl et al., 2004; Burkholder et al., 2006; Howarth and Marino, 2006; Howarth and Paerl, 2008; Conley et al., 2009; Paerl, 2009). The synthesis provided here bears on this argument in several ways. In many estuarine systems, N is no longer the limiting nutrient; it is the excess of N loading that is

of concern, not its lack of supply. Reductions in P have indeed reduced chlorophyll *a* levels in many systems, and this change in phytoplankton biomass has frequently been referred to as oligotrophication. Moreover, the shift to an alternate stable state does not a priori mean that the system is returned to its natural, un-eutrophied state, because that system may be much more susceptible to invasions of non-indigenous species. While individual species and processes respond to single nutrients, the relative proportion of N and P collectively alters metabolism, species composition, and food webs. Nutrient ratios may not effectively structure phytoplankton communities (with the exception of N_2-fixing cyanobacteria favored when N:P ratios are low), but they exert a strong regulatory control on food webs, biogeochemistry, and ecosystem structure *as a whole*.

(3) In what has become a much-referenced study in a very short period of time, Duarte et al. (2008) discussed the pathways of return of an ecosystem following nutrient removal—the "Return to Neverland" (sensu the children's story of Peter Pan and Wendy). They surveyed the literature for systems that have undergone nutrient loading and nutrient reductions to determine if there were common patterns. The trajectories of response were complex and varied. Duarte et al. attributed this to "shifting baselines," recognizing that systems have changed due to invasions, extinctions, overfishing, climate change, and other factors; thus, any expectation that the system will return to what it was decades before is a flawed assumption. They did not, however, differentiate those systems where stoichiometry had been altered. Despite the difficulty in predicting exactly how individual systems will respond, Duarte et al. (2008, p. 6) underscored that "efforts to reduce nutrient inputs to eutrophied coastal ecosystems have indeed delivered important benefits by either leading to an improved status of coastal ecosystems or preventing damages and risks associated to further eutrophication." A stoichiometric perspective may aid the understanding of how systems can actually return to a new—or altered—stable state.

(4) Global change patterns suggest that acidification of the oceans and its effects on physiology and biodiversity is a major emerging issue (e.g., Fabry et al., 2008; Hendriks et al., 2010; Kroeker et al., 2010; Vézina and Hoegh-Guldberg, 2008 and references therein). Shown here, as well as in many other reports (Pedersen and Hansen, 2003a,b; Søderberg and Hansen, 2007), highly productive aquatic systems are, instead, sustaining alkalinification. As suggested here, alkalinification may be another consequence of altered N:P ratios and the comparative ability of macrophytes to thrive under these conditions. The consequences for biogeochemical and related trophic dynamic changes at high pH are as large as those at reduced pH values. The range of pH fluctuations under highly productive systems, up to several pH units, is much higher than what is occurring and expected under acidification. There is a pressing need to better understand effects of variable pH must be better understood across the range of environmentally relevant pH values, including the alkaline range.

(5) One of the most common "currencies" of trophodynamic studies is C. Many studies normalize rates or mass to C. When food quality (i.e., nutritional content) is linked to food web outcome, however, feedback effects and nutrient biogeochemical processes also play large roles in species success. The findings here suggest that strengthened insights may be gained by use of additional denominators—that P and N "currency" yields insights not found with C "currency." While productivity is a function of C, community composition is more strongly linked to N and P. Conceptualizing all change as a function of C transfer and productivity can lead to a flawed conclusion that productivity, biomass, and species composition are all regulated by a single element (McIntyre and Flecker, 2010). Similarly, many trophic interactions, such as, for example, rates of growth or fecundity, are interpreted in the context of the requirements by grazers for acquisition of particular fatty acids, as a measure of the food quality of algae (e.g., Ågren et al., 1990; Coutteau and Sorgeloos, 1997; Weers and Gulati, 1997; Brett and Müller-Navarra, 1997). Some diatom species produce certain highly unsaturated fatty acids that are essential for zooplankton reproduction (reviewed by Kilham et al., 1997), while flagellates generally produce different fatty acids than diatoms (Olsen, 1999). Moreover, some cyanobacteria greatly reduce their phospholipid content in relation to P stress (Van Mooey et al., 2009), while some green algae have been shown to have higher lipid content under P limitation (e.g., Kilham et al., 1997). Cellular biochemical constituents are strongly influenced by the elemental composition of the cells, and relationships between these indices of food quality and elemental stoichiometry should be explored.

(6) Cyanobacteria may do well at both ends of the Redfield spectrum. Most of the previous focus on P reductions has been based on the assumption that N limitation will lead to cyanobacterial blooms, because many cyanobacterial species are capable of N_2 fixation; thus, if N-limiting conditions do not occur, cyanobacteria blooms may be reduced or avoided (e.g., Downing et al., 2001). However, *Microcystis* often occurs in *high* N:P ambient conditions, making it an enigmatic bloom former under the prevailing assumption that high N:P will drive the ecosystem away from cyanobacteria. Its success apparently is a function of its ability to either efficiently garner its requisite P or reduce its P requirement. Stoichiometric homeostasis (Figure 4) may be yet another explanation for release of nutrient-rich (or, in some cases, C-rich) toxins, not only by *Microcystis* but potentially by other harmful algal species, such as dinoflagellates.

(7) Various indices and metrics have been developed to measure eutrophication status (e.g., Llansó et al., 2003; Corbett et al., 2005; Buchanan et al., 2005; Lacouture et al., 2006; Bricker et al., 2008; Williams et al., 2010; US EPA, 2009).

However, virtually all of these indices are measures of the classic symptoms of eutrophication—increase in chlorophyll *a*, decline in SAV, extent of hypoxia, or harmful algal blooms (HABs). There are as yet no quantitative indices for the impacts of altered stoichiometry. Application of the traditional eutrophication indices will lead to the erroneous conclusion that these systems are *not* nutrient stressed. A new suite of indicators needs to be developed to more accurately characterize these systems. Such indicators will need to vary, depending on which end of the stoichiometric continuum a system may lie. For systems with high N:P ratios, these indicators could include extent of coverage of SAV by invasive macrophytes, decline in chlorophyll *a*, extent of cyanobacteria blooms, bivalve invasions, piscivore/planktivore abundance, calanoid/cyclopoid ratios, and sediment release of P and N, as examples.

(8) The alternate stable states that have been documented here and in comparative systems should be considered in light of additional societal considerations about which state is preferred. The Bay Delta management arena has coped with societal implications of water use with regard to protections of an endangered species. Shown here is a dichotomy of stable states of fish communities. If stoichiometry is indeed an important regulator of trophodynamics, to save the delta smelt (i.e., to restore large populations of it) will require that the system be adjusted to have many characteristics of a more classically defined eutrophic system, with higher chlorophyll *a* levels, higher turbidity, less benthic vegetation, and fewer largemouth bass. Most coastal communities that are coping with systems in altered stable states are attempting to shift to a system with more piscivores, not fewer, and clearer conditions, not more turbid water.

(9) Regulation of a single nutrient without recognition of the role of nutrient stoichiometry simply serves to displace in space the impacts of eutrophication (Fisher et al., 1992; Hagy et al., 2004; Paerl et al. 2004). While production and chlorophyll *a* biomass may be held in check in the river or estuary due to P limitation, N is displaced downstream where it eventually intercepts adequate levels of P to form blooms, either in the estuarine reach of the system—or even offshore (Figure 39). Such an effect has been documented for the Neuse River Estuary, the mesohaline reach of Chesapeake Bay, and the southern Baltic Sea in the Sweden archipelago region; eutrophication effects increased in these systems when P reduction, but not N reduction, was imposed upstream (Fisher et al., 1992; Paerl et al., 2004). Many marine HABs are increasing (Anderson et al., 2002; Glibert et al., 2005; Heisler et al., 2008), and increasingly these changes are being related to nutrient changes, even for those species that were previously thought to be unrelated to nutrient pollution (Burkholder et al., 2008). For example, the classic "red tide" former, *Noctiluca scintillans*, was recently found to be associated with offshore transport of excess N, mediated through N cycling and trophic transfer (Harrison et al., 2011). Thus, in a transect from an N-impacted river to the sea, stoichiometric proportions change significantly, and when P is controlled upstream, algal blooms are displaced either downstream or offshore. Dilution does not solve the problem, it just displaces it.

Recommendations for Further Study

While compelling, the ecological stoichiometric model raises many questions that need further analysis in the San Francisco Estuary. The synthesis provided herein is based on a reconstruction of biogeochemical and trophic interactions based on historical data and basic knowledge of biogeochemical processes and organismal physiology. Using comparative systems, it was shown that similar dynamics have developed in other systems affected by similar stressors. However, regulation of the food web by nutrient controls is directly testable, and there is much that needs to be explored to test these relationships directly.

In 1985, Cloern and Nichols outlined a number of research questions regarding the importance of nutrients and nutrient processes that were understudied in the San Francisco Estuarine system. Although progress has been made on some of these issues, many remain. These include, "sediment dynamics and transport, primary production of benthic microalgae, virtually all aspects of microbial ecology and biogeochemistry, the nature and role of microzooplankton, sources and fates of toxic contaminants (particularly organic compounds), nutrient budgets, and riverine inputs of organic material" (Cloern and Nichols, 1985, p. 236).

In 2011, many of the same research questions can be outlined, including:

(1) What are the dynamics of sediment nutrient fluxes, and how do they vary spatially and seasonally within the Bay Delta? How do they vary with freshwater flow?

(2) What are the dynamics of the organic sources of nutrients, and how does their stoichiometry compare to the inorganic forms presented here? How do they vary spatially and temporally? How do they contribute to the nutrition of the primary producers?

(3) How do rooted versus floating invasive macrophytes differ in their alteration of biogeochemical fluxes of nutrients, and how does this vary with nutrient stoichiometry? How does the metabolism of these plants compare to that of native vegetation?

(4) To what extent are bacteria and microzooplankton stoichiometrically constrained, and how do their changes relate to water column nutrient stoichiometry?

(5) What is the biomass stoichiometry of the fishes of the Bay Delta? Do fish of varying species change in growth rate and size in relation to varying quality of nutrients in their diet?

(6) Do stoichiometric changes or changes in flow (or salinity) have a greater effect on fish metabolism/macroinvertebrate metabolism?

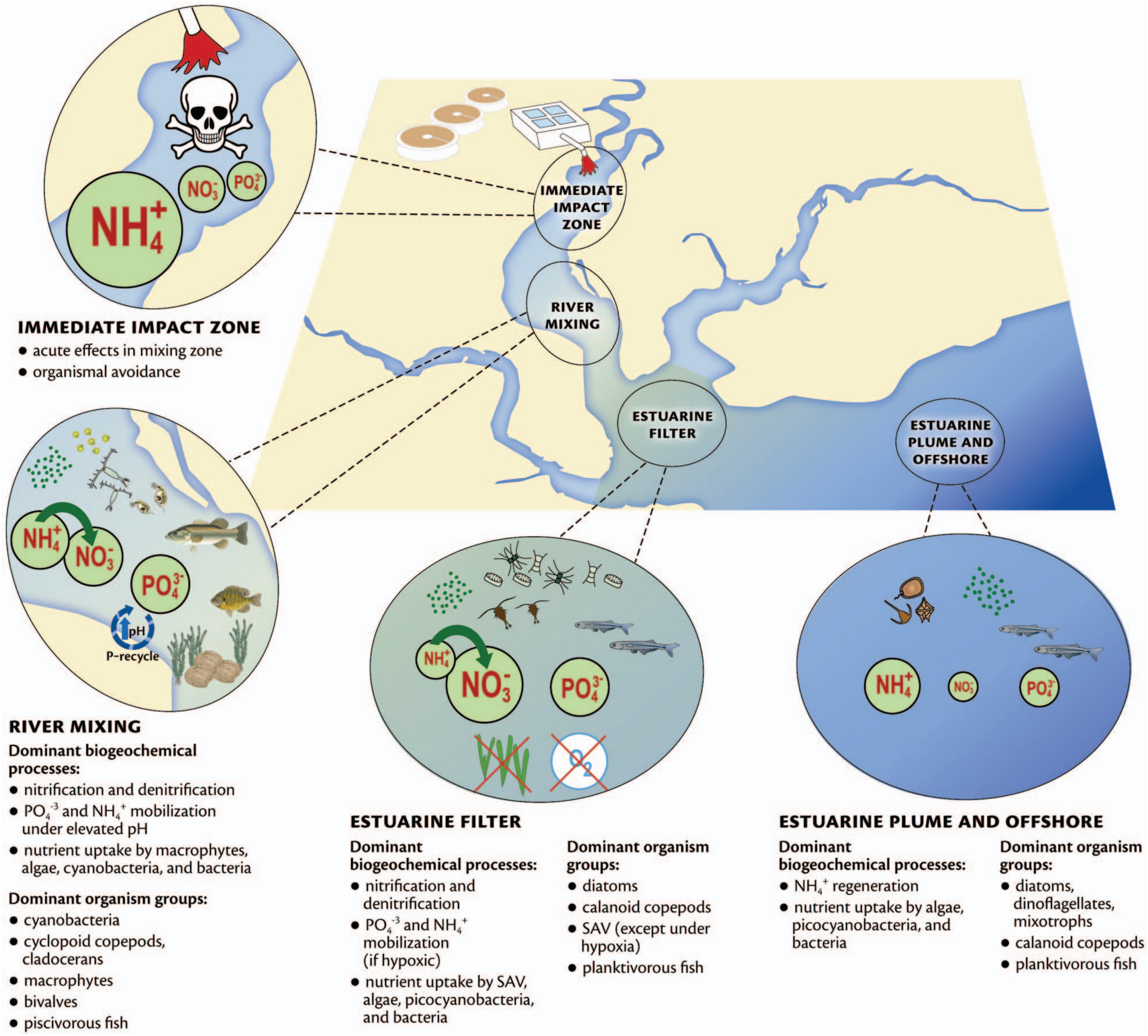

Figure 39 Conceptual diagram of a generalized estuary affected by high NH_4^+ loading from a point source discharge but with reduced P loads. The immediate impact zone has the potential to have strong negative impacts on organisms, either through direct toxicity or indirect inhibition effects. As the NH_4^+ moves downstream, processes such as nitrification (depicted as an arrow from NH_4^+ to NO_3^-) may convert substantial amounts of N from NH_4^+ to NO_3^-. If macrophytes are common in this reach of the system, recycling of P from the sediment may result in increased P availability, although numerous organisms may effectively take this up and sequester this P. Moving further downstream into the brackish estuarine zone, nitrification may continue, resulting in increased availability of NO_3^- relative to NH_4^+. Together with P release from the sediments, and/or with inputs of P from oceanic sources, blooms of diatoms or other algae may occur in this region, and the excessive production may result in hypoxia, seagrass loss, etc. The effectiveness of the estuarine filter (sensu Cloern 2001) will depend on the size of the estuarine, residence time, depth, and many other factors. When N loading is very high, it will not all be effectively taken up in the riverine and estuarine segments and will be exported offshore. The export may be in the form of dissolved (inorganic or organic) or particulate N. When sufficient P is available in offshore sources, additional blooms may develop. A succession of blooms may also occur, with increasing importance of mixotrophic dinoflagellates expected in such a progression (color figure available online).

(7) How does the stoichiometry of the invasive fauna compare with that of native species?

(8) What are the synergistic effects of stoichiometric changes in ambient nutrients and other stressors on the Bay Delta food web, such as changes in temperature, pH, or light?

Answers to these questions, attainable through studies in controlled laboratory or mesocosm settings or field measurements, would greatly advance understanding about the factors controlling the food web of San Francisco Estuary and would also advance the knowledge base and tools for managers to make informed decisions regarding the future of the Bay Delta.

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NOTE ADDED IN PROOF

Sobota et al. (2011) have estimated multiple sources of P inputs to the Bay Delta based on spatially explicit information on fertilizer, livestock, agriculture and human population. Human sewage was the dominant source in the Upper Sacramento. They underscore that more biogeochemical information on P sources and export is needed for this system.

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Ecological stoichiometry and its implications for aquatic ecosystem sustainability

Patricia M Glibert

Aquatic ecosystems are increasingly stressed not only by increased nutrient loads (eutrophication) but also by changing forms and proportions of nutrients. Nutrient enrichment, composition and stoichiometry interact with aquatic food web dynamics in complex ways. Both algal species composition and emergent properties within species change with changing nutrient composition, in turn affecting food webs at all levels. Consumers further regulate – and may even accelerate – discrepancies in nutrient stoichiometry by various feedbacks, release, and recycling pathways. Stoichiometric regulation of aquatic ecosystem structure also occurs at the sediment interface via altered biogeochemical processes and benthic food webs when nutrient composition changes. Thus, multiple feedbacks serve to alter food web structure when nutrient loads are altered. Such feedbacks may also lead to conditions conducive to invasive species and altered stable states as illustrated for the San Francisco Bay Delta and the Rhine River.

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Introduction

Much has been written about the eutrophication of lakes, estuaries and coasts ([1••,2,3] and references therein). Anthropogenic activities have significantly altered nutrient loads and their composition, in turn profoundly affecting ecosystem health [4]. For example, well-documented effects of increased nutrient loads and eutrophication include loss of biodiversity, increased harmful algal blooms, and development of dead zones [5,6]. Beyond eutrophication, changes in nutrient loads are impacting ecosystem dynamics in complex ways. Changes in nutrient form (chemical state, oxidized vs reduced, organic vs inorganic, dissolved vs particulate) and the proportion of different elements (C, N, P, Si, etc.) have both proximal and ultimate effects on ecosystems (*sensu* [7]). The stoichiometry (proportions) of nutrients, especially nitrogen (N) and phosphorus (P), in many aquatic systems is changing as a result of both increasing nutrient loads (often dominated by N) on the one hand, and management efforts focused on single nutrient control (often P) on the other. At the primary producer level, many of these effects are well understood, framed largely in the concepts of Leibig's law of the minimum and Redfield stoichiometry (reviewed by [8•,9,10•]). At the proximal scale, here defined as the scale of growth of primary producers, nutrient form and concentration affect the cell physiological processes of uptake, assimilation, and those, in turn, regulate the internal concentrations that regulate growth (e.g. [11]). At the ultimate scale, the total load and balance of nutrient elements have effects that propagate through the food web, with the potential of transforming ecosystems to new stable states. The regulation of food web structure by nutrient stoichiometry is further controlled by the various and complex feedbacks, release, and recycling pathways that that are all fundamentally constrained by nutrient load, form or stoichiometry. Just as different elemental ratios may affect the composition of the primary producers, different nutrient requirements of higher trophic levels will have an impact on their ability to thrive as community composition changes at the base. The latter is the emphasis of this brief communication.

Stoichiometry, biotic feedbacks, and biogeochemistry

An ecological stoichiometric approach is based on the transfer of elements through the food web, not just the flow of carbon (C) [12••]. Generally, homeostatic mechanisms keep the acquisition of materials and energy in balance with the cellular growth demands of primary producers and the general consistency of Redfield stoichiometry in phytoplankton is corroborative (e.g. [10•]). Ecological stoichiometry recognizes that at the base of the food web, the elemental composition of the primary producers is affected by nutrient composition whether nutrients are limiting or not. While the total nutrient load of the nutrient considered to be limiting for phytoplankton production may control overall biomass, the composition, both in form of nutrients and the proportion of different nutrient elements affects the composition of the primary producers. When nutrient loads change in amount, form or proportion, cellular adjustments in acquisition efficiency lead to altered emergent properties such as the proportions of ribosomes, enzyme activities, gene regulation, cellular pigmentation complement, and

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cellular elemental composition [12••]. These properties have implications for competition and species success, leading, eventually, to changes in species dominants and biodiversity. In addition, properties such as lipid composition, toxin production, cell membrane thickness, and other chemical constituents, which are also, at least partly, functions of cellular elemental availability, can alter the quality of food for consumers, in some cases turning 'good' food to 'bad' [13,14]. Production of toxins in algae, for example, often occurs when nutrient stoichiometry is not in classic ('Redfield') stoichiometric proportions [14,15]. Toxic species can be harmful to higher trophic levels, disrupting normal ecosystem function. The dominance of such algae can result in a failure of normal predator-prey interactions, which in turn enhances the transfer of nutrients that sustain such species at the expense of competing algal species [16–18].

While primary producers may be flexible to some degree in their elemental composition [19••,20], heterotrophs are typically far less flexible [10•,12••,21••]. The nutritional quality of the food at the base of the food web affects all aspects of the abilities of consumers to meet their nutritional and reproductive demands. Nutrient stoichiometry and food quality can have differential effects on consumers depending on their life stage, for example, larval or adult [22–25]. Larvae would be expected to have higher P demands, for example, than adults, owing to their higher growth rates [22]. Heterotrophs typically maintain a more strict stoichiometry than phytoplankton through their various excretion and release mechanisms [12••,26], and the relationship between their biomass elemental requirements and the proportion of those elements in their food determines the extent to which they are a sink or a source of N, P or C [12••,27]. In general, as one moves up the food web, stoichiometric constraints on grazers increase, as does the organismal requirement for P, owing to fixed stoichiometry in body tissue, especially bone [12••]. Heterotrophs thus can exert significant control on the N and P available for primary producers [12••,28].

The biota thus modify the environment through nutrient uptake and regeneration which differs from species to species based on their elemental requirements and the nutrient substrates available to them as dissolved nutrients or as food. In addition to the biotic feedbacks and regulatory controls whereby individual organisms maintain their stoichiometry under mass balance constraints, at the ecosystem level, growth of different species also modifies the physical and chemical environment through alterations in physical habitat (e.g. turbidity, flow), light, oxygen, pH, as well as substrate availability. These factors can alter the pathways by which nutrients are released from the sediment, or the rates by which they are transformed in the sediment or water column by such processes as nitrification, denitrification, anammox, or dissimilatory nitrate reduction to ammonium (DNRA). In eutrophic systems, increased algal productivity may lead to depressed water column oxygen which may result in increased recycling of N and P by changes in redox potential, or pH [29••,30,31]. These fluxes can positively reinforce an ecosystems' degradation trajectory, as suggested to be the case for the Chesapeake Bay [31]. By contrast, in systems with a reduced nutrient load, lower algal abundance in the water column, higher light, and higher redox potential may help to reinforce higher rates of nitrification and denitrification, leading to nutrient removal and potentially eutrophication reversal [31]. Biogeochemical pathways together with homeostatic control serve to provide the mechanism(s) whereby nutrient dynamics support trophodynamic structure. Positive reinforcing feedbacks of biogeochemistry and homeostasis shift ecosystems to new stable states; such shifts can be gradual or abrupt and communities may not return to their original state once the disturbance (in this case, altered nutrient loads) is removed.

Altered ecological stoichiometry and associated ecological feedback mechanisms may also help to explain the potential for a system to support the growth of organisms previously not found in an area, that is, biological invasions. While changes in climate, land-use and other factors have long been recognized to be related to a system's susceptibility for invasive species to thrive, so too is the possibility that altered nutrient loads may make an environment more suitable for species with different nutritional requirements [29••]. Such a suggestion does not negate the importance of external vectors bringing invaders to a new area, but nutritional loads, and the associated ecological feedbacks that may alter habitat, adds a mechanism to explain why some shifts occur when they do, and when and why particular species are successful in new environments [29••].

Examples from comparative systems

Two estuarine examples illustrate the important feedbacks between changes in nutrient loads and their stoichiometry, biogeochemistry, food web structure and potential for biological invasions. The San Francisco Bay Delta, a heavily modified and anthropogenically impacted estuarine system, has had major changes in nutrient loads over the past several decades ([29••,32] and references therein). In particular, increases over time in the N:P ratio of the major nutrient loads have been attributed, at least partly, to increases in wastewater N and removal of P from laundry detergents [29••]. Coincident with, and related to, these changes are declines in water column algal biomass (as chlorophyll *a*), a shift in the dominant zooplankton species from the calanoid *Eurytemora affinis*, to the invasive cyclopoid *Limnoithona tetraspina*, as well as invasions of the Asiatic clam, *Corbula amurensis*, the macrophyte, *Egeria dense*, and various species of centrarchid fish [29••]. *Egeria dense* is thought to do particularly well under increasing water column N:P

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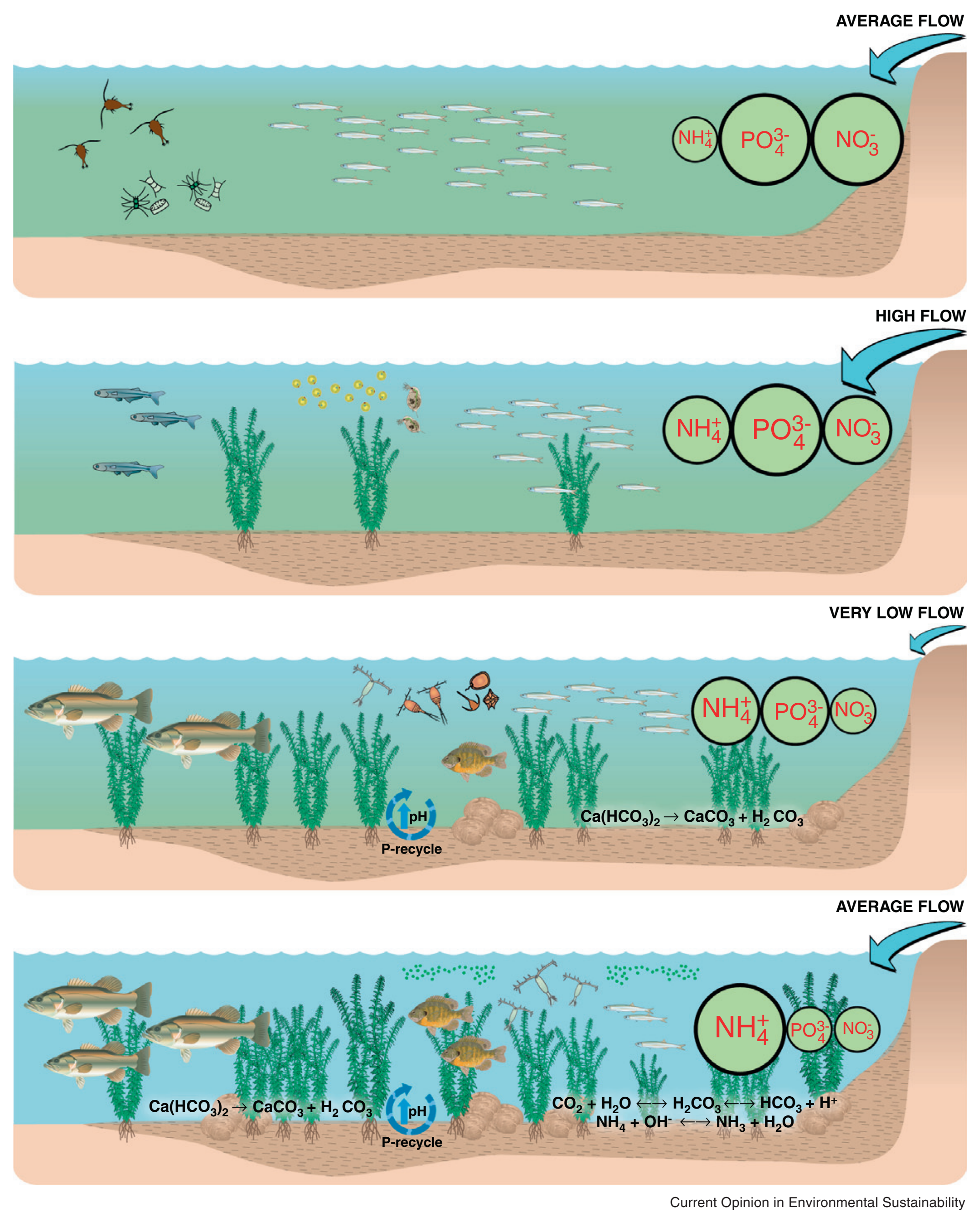
Figure 1



Conceptual depiction of the change over time in major nutrients, flow, dominant biogeochemical processes, and the food web of the San Francisco Bay Delta illustrating how multiple feedbacks serve to alter food web structure when nutrient loads are altered. The first panel represents the period from 1975 to ~1982, when flow was low, and diatoms were the dominant phytoplankton, and the calanoid copepod *Eurytemora* was the dominant copepod, and pelagic planktivorous fish were common. The second panel represents the period from ~1982 to 1986 when flow was high, and NH_4^+ was increasing. During this period the food web began to change. Under very low flow conditions, depicted by the third panel, and representing ~1987–1995, the NH_4^+ load was high but PO_4^{3-} began to decrease. The food web also began to change significantly, with changes in the dominant phytoplankton and zooplankton, increasing abundance of macrophytes, increased importance of sediment nutrient processes, and increase in piscivores. Finally, post 1995, NH_4^+ loads remain high, while PO_4^{3-} loads have decreased. Sediment biogeochemical processes are of increasing importance in nutrient processing, macrophyte production is important and piscivorous fish have increased.Reproduced from Glibert *et al.* [29••] with permission of the publisher.

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loads because it can access P through the sediments, and can tolerate high N, especially in the form of NH_4^+, in the water column. It also serves as an 'ecological engineer', decreasing nutrients through uptake, reducing turbidity by trapping sediments, and providing refuge for zooplankton and habitat for fish such as largemouth bass [33]. More importantly from a chemical perspective, it is able to use bicarbonate effectively though a well-developed carbon-concentrating mechanism (e.g. [34]). The consequence is that it does not become C-limited even under periods of high productivity, in turn elevating pH on a diel basis in the surrounding water as it grows, in some cases substantially. Once pH is elevated, the fundamental physical–chemical relationships related to P adsorption–desorption in the sediment change, as does N biogeochemistry [35,36]. Moreover, under increased pH conditions, the biogeochemistry of calcification is altered, increasing the potential for calcification and the growth of calcifying organisms. The change in the abundance of the clam *C. amurensis* from the time of its introduction in the mid-1980s to 2005 has been shown to be highly and positively correlated to the increase in total N:total P ($r^2 = 0.46$; $n = 20$; $p < 0.01$; all data log transformed), and the average annual abundance of this species has also been found to be highly and positively correlated with mean annual average pH in the estuary ($r^2 = 0.64$; $n = 19$; $p < 0.01$; species abundance data log transformed) [29••]. Thus, over time nutrient loading changes, biogeochemical changes and foodweb changes were intertwined (Figure 1).

The River Rhine presents a parallel example [37,38]. From 1977 to 2005, total P loads declined over 6-fold owing to reductions in wastewater loading from municipal and industrial facilities and the total N:total P ratio increased 3-fold, in turn resulting in an 8-fold decline in water column chlorophyll *a* [38]. Cumulative non-indigenous species increased from ~20 to >50 during these years, a rate of accumulation higher than seen in any year of record, dating back to 1825 [37]. Most of these species were molluscs (22% of total) and crustacea (51% of total); among the molluscs, the most abundant were the clam *Corbicula fluminea* and the mussel *Dreissena polymorpha* (zebra mussel) [37]. The annual rate of change in number of animal non-indigenous species and the rate of change in the ratio of total N:total P in the water column over this ~30-year time period are highly and positively correlated ($r^2 > 0.40$; $n = 28$; $p < 0.05$). In addition, invasive macrophytes, including *E. dense*, are increasingly common in the Rhine [39], as they are in the San Francisco Bay Delta.

While there are many vectors that may deliver non-indigenous species to new areas, there is no question that altered biogeochemical composition of the water column, and the associated shifts in primary production can set in motion a cascade of changes that facilitate the success of new species. Thus, both the Rhine and the Bay Delta had similar types of ecosystem changes following changes in N:P stoichiometry: significant declines in chlorophyll *a*, invasions of *E. dense*, bivalve clams, and changes in crustacea. These examples illustrate that when P is reduced relative to N, and when the system production becomes more benthic in nature, new dominants may emerge. In the case of filter-feeding molluscs, they, in turn, may help to maintain the new water quality condition by enhanced filtration of the water column.

Conclusions and implications

Nutrient stoichiometric control of ecosystem structure and sustainability must be viewed within the context of other factors in the environment, including the multiple stressors that now impact systems, as well as the scale (spatial, temporal and organismal; proximate or ultimate) on which the system is being examined. Trophodynamics and biogeochemical processes are fundamentally coupled, but are also fundamentally constrained by the availability and composition of elements relative to the needs of the organisms. Ecological stoichiometry affects ecosystems by setting elemental constraints on the growth of organisms, with several important implications for the health and sustainability of aquatic systems. Stoichiometric imbalances may accelerate transformations of nutrients or may alter the processes by which nutrients are cycled in the ecosystem, further altering nutrient availability or form for primary producers [28,40]. Food *quality* is linked to food web outcome via feedback effects and nutrient biogeochemistry, key processes determining biodiversity. Models of ecosystem function based on classic nutrient or growth kinetic relationships, or flow of single elements (i.e. C), are ill-suited to capture the complexities of stoichiometric effects on ecosystems [41]. Although far more complex than single currency models, multiple currency models and ecological stoichiometric concepts should be among the considerations that should go into a new generation of ecosystem models [11,29••,42•,43].

Ecological stoichiometry should be incorporated into our thinking, management, and modeling of the dynamics of nutrient-impacted systems. Imbalances in stoichiometry may have impacts on ecosystems even at nutrient loads normally taken to be saturating or supersaturating. The effect of stoichiometric constraints has implications, for example, on bioenergetics and all aspects of fish nutrition, both from a basic ecological perspective as well as applied, including aquaculture [21••,44]. Moreover, ecological stoichiometry bears significantly on the debate of whether aquatic ecosystem restoration efforts should focus on P removal, N removal, or both (e.g. [45,46,47••] and references therein). Single nutrient removal strategies drive ecosystems into states of stoichiometric imbalance [29••]. Imbalances in stoichiometry may destabilize the dynamics of consumers, shifting systems to new conditions. Single

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nutrient removal strategies may have unintended consequences for aquatic ecosystems.

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From limitation to excess: the consequences of substrate excess and stoichiometry for phytoplankton physiology, trophodynamics and biogeochemistry, and the implications for modeling

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ABSTRACT

Current parameterization of several important physiological rates using rectangular hyperbolic saturation formulations is inadequate to capture our expanding understanding of the dynamic regulation of nutrients and energy at the primary producer level across all substrate levels, from limiting to super-saturating. Nutrient regulation by primary producers can affect chemical composition, in turn affecting predator–prey interactions and biogeochemical feedbacks in complex foodwebs. Anthropogenically altered nutrient loads are accentuating these challenges by altering nutrient stoichiometry. Using examples derived from the development of phytoplankton physiological dynamic regulation, the case is made that dynamic regulatory concepts are relevant at all levels of ecosystem regulation, that elemental stoichiometry must be considered in physiological, trophodynamic and biogeochemical constructs, and that the classical notion that nutrients and nutrient stoichiometry are only regulatory for physiology when at the limiting end of the spectrum must be laid to rest. Advancing models will require new emphasis on physiology including both dissipatory regulation and assimilatory regulation and the feed-back mechanisms between them.

1. Introduction

Ecosystem modeling has advanced tremendously in the past decade- with increasing sophistication in our ability to visualize large data sets, conceptualize complex interactions and formulate predictive scenarios based on model ensembles. Operational forecasting models for many aspects of global change now range from the regional to the global ocean. The need for predictive models is large and increasing, particularly with climate change and the increasing observations of acidification and harmful algal blooms (HAB).

Models depend on parameters that are not always easily measured or available and as a result, mass fluxes, dynamics, and physiological variables are often not adequately captured. Traditional mass-based models (often either single nutrient, N or C) are generally relatively simple and operate using classic uptake kinetic relationships. Yet, even these classic relationships are poorly characterized for many species or are highly variable under different growth conditions (Glibert and Burkholder, 2006). Several authors (e.g., Allen and Polimene, 2011; Flynn, 2010) have recently argued the need for a new generation of plankton models based on emerging knowledge of dynamic cellular and ecophysiological behavior. Here we add our voice to this chorus. Much has been learned about organismal adaptation and physiological responses to variable environments — from phytoplankton growth to competition, mixotrophy, allelopathy, prey switching and/or prey rejection, and the relationships between these processes and various abiotic factors such as temperature, pH, and light. Physiological traits of marine organisms are now being applied in models of emergent marine biodiversity (Follows et al., 2007) and some new-generation, mechanistic population dynamic models and three-dimensional ocean biogeochemical models incorporate phytoplankton functional groups, multiple limiting nutrients, flexible elemental composition, and iron limitation (e.g., Baird and Emsley, 1999; Klausmeier et al., 2004; Le Quéré et al., 2005; McGillicudy et al., 2010; Moore et al., 2004; Ramin et al., 2012). These latter approaches have made significant advances but they still often depend on poorly characterized physiological relationships.

Flynn (2010) highlighted the inability of classic kinetic relationships and fixed elemental stoichiometric concepts to capture phytoplankton interactions when cells are nutrient stressed. In fact, it has been argued that these models are unsuitable, or even dysfunctional for descriptions of algal nutrient uptake or growth under more natural, variable nutrient conditions (Flynn, 2005, 2009; Goldman and Glibert, 1983). This is, in part, due to the fact that nutrient stress develops before the nutrient becomes completely exhausted (Flynn et al., 1999, p. 356). Adding to these difficulties is the recognition

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that both nutrient limitation and nutrient saturation result in dynamic phytoplankton physiological changes which have consequences for chemical composition which, in turn, affect trophodynamics.

This later observation, that nutrient saturation may be a cellular stress, is pertinent to those systems that have chronically high nutrient concentrations resulting from eutrophication. However, conventional nutrient kinetic models that incorporate a saturation response would dictate that nutrients cannot be regulatory at saturating concentrations with respect to rate processes, such as growth rate (e.g., Reynolds, 1999). Here, this premise is challenged.

The central premise of this paper is that the use of classic, saturation formulations used to parameterize physiological rates are inadequate for modeling the dynamic regulation of nutrients and energy at the primary producer level across all substrate concentrations and that complex dynamics at the physiological scale has important implications in understanding predator–prey interactions and biogeochemical feedbacks. That is, the reductionist approach of quantifying the parameters defining limitation and saturation as fixed entities constrains both our understanding of the dynamic regulation of physiological and metabolic processes across all substrate or resource levels and hampers our ability to capture this dynamic regulation in complex food web models. Current parameterization of kinetics and rate processes is challenging for both physiologists and modellers because of 1) experimental and methodological difficulties in "getting the curve right", especially in light of our advancing tools; 2) failure to consider changes in rates or organismal physiology beyond the concentration range that typically bounds the limit of saturation of the rate process; 3) lack of consideration of more than one element or substrate; and 4) difficulties in relating dynamically changing physiology and stoichiometry to food webs and to biogeochemical feedbacks. The goal of this paper is to underscore that advances in physiology are fundamental to achieve advances in models at various scales, that consideration of dynamic regulation and stoichiometry are keys to these advances, and to emphasize how anthropogenic nutrient loads are accentuating these challenges by altering nutrient stoichiometry.

2. Rate processes as a function of substrate availability

2.1. A "curve for all reasons"

Phytoplankton physiologists often measure, and modelers often parameterize, processes as a function of substrate availability by a curvilinear function, a rectangular hyperbola (Fig. 1). Growth as a function of nutrient concentration (Monod, 1942), nutrient uptake as a function of external nutrient availability (Menten and Michaelis, 1913), nutrient uptake as a function of cellular internal nutrient concentration (Droop, 1973, 1979), and photosynthesis as a function of irradiance are all examples of such formulations. For grazers, similar relationships define grazing or ingestion as a function of food availability. Indeed, the rectangular hyperbola has been termed "a curve for all reasons" (Rao, 2000; Table 1). In each of these formulations, a maximum (saturating) rate is identified, as is a half-saturation constant or an index of the concentration at which the rate plateaus (e.g., I_k for photosynthesis), and the rate of change (initial slope) are characterized (Fig. 1). In some cases, for example, photosynthesis models, an inhibiting term may be incorporated. These basic functions are central to many plankton models, such as nutrient–phytoplankton–zooplankton models (e.g., Franks, 2002).

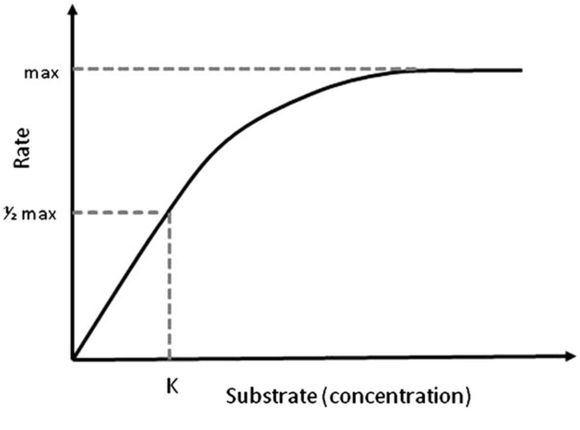

Fig. 1. The classic kinetic rectangular hyperbola indicating the change in a rate or process as a function of substrate availability.

The concept of a saturating relationship in relation to "resources" is also applied at the population level. Applying the Verhulst model of population dynamics,

$$dN/dt = rN(1-(N/K)) \quad (1)$$

"r" selected species are those with rapid growth rates, whereas "K" selected species are slower-growing, but are adapted to living at densities close to carrying capacity, K, of the environment (Verhulst, 1938). In nutrient-rich aquatic environments, r-strategist phytoplankton are typified by bloom-forming diatoms, whereas K-strategists dominate in more nutrient-poor, "mature" systems, typified by dinoflagellates (many of which are mixotrophic) (Flynn et al., in press).

2.2. Challenges of getting the curve right

Models must balance simplicity with realism and complexity. Saturating response curves have a great appeal because they contain not only an efficiency parameter, but a constraint on the maximum rate, which is necessary to satisfy inherent biological metabolism (i.e. growth rate cannot be unconstrained) (Rao, 2000). For reasons of computational efficiency and/or availability of calibration data, many models operate with a single set of kinetic parameters or with the simplifying assumption that a single efficiency parameter (i.e., K_s or I_k) or rate (i.e., V_{max} or P_{max}) is applicable to all species or all conditions. There are several major challenges to "getting the curve right". The first is adequately characterizing it and understanding its variability (Burmaster and Chisholm, 1979; Goldman and Glibert, 1982, 1983; Gotham and Rhee, 1981; Morel, 1987; Rhee, 1973). Kinetic relationships ranging from enzymatic control to *in vivo* rates exhibit variation and this variation increases in complexity at higher levels of organization as processes of cellular control over enzyme synthesis and control of auxiliary factors become part of cellular function. The fact is, there is no higher level process that can be fully constrained by a single substrate kinetic curve, even at the simplest level of enzyme reactions. The challenge is to identify a relationship that is representative of the process under relevant conditions and to identify the family of curves that envelop the response of individual species or communities, depending on model purpose. Toward this end, it is necessary to define the pertinent scale (typically temporal) and relationships between kinetics measured at one scale and the extent to which they may be applied to a different scale (e.g., uptake kinetics applied to growth kinetics; Goldman and Glibert, 1983). Ecosystem modeling, by its nature, deals with longer temporal scales compared to the scales on which biochemistry and physiology operate. Nutrient kinetic relationships or photosynthesis rates are typically determined on the physiological scale, but the relationship of those kinetics is 'filtered' by cell metabolism and cellular functions (e.g. nutrient storage or release) that ultimately influence the transfer of material at the ecosystem level.

The second challenge is that many kinetic or process relationships are difficult to measure well, especially under in situ conditions, and that measurements made with one technique are not necessarily equivalent to those made with another technique, leading to wide uncertainly in what kinetic parameters to apply in models. For example, the measurement of productivity may be made by use of ^{14}C, ^{18}O, or

Table 1
Examples of applications of the rectangular hyperbola in plankton ecology.

Process	Independent variable	Dependent variable	Formulation	Notes
Enzyme kinetics	Substrate concentration	Enzyme rate	$V = V_{max}[S/(Km + S)]$	V is the specific activity rate; V_{max} is the maximum activity rate; S is the substrate concentration; Km is the enzyme half-saturation constant (Menten and Michaelis, 1913)
Phytoplankton growth	Nutrient concentration	Growth rate	$\mu = \mu_{max}[(S/(K\mu + S)]$	μ is the specific growth rate; μ_{max} is the maximum specific growth rate; S is the substrate concentration and Kμ is the half-saturation for growth (Monod, 1942)
Nutrient uptake (external)	Nutrient concentration (external media)	Nutrient uptake rate	$V = V_{max}[S/(Ks + S)]$	V is the specific uptake rate; V_{max} is the maximum uptake velocity; S is the substrate concentration; Ks is the half-saturation for uptake (Dugdale, 1976)
Nutrient uptake (internal)	Nutrient concentration (cellular)	Nutrient uptake rate	$\mu = \mu_{max}[1 - (Kq/Q)]$	μ is the specific growth rate; Q is the cell quota; Kq is the minimum cell quota; μ_{max} is the unattainable μ at infinite Q (Droop, 1973, 1979)
Photosynthesis	Irradiance	Photosynthesis rate	Variable formulations which may or may not include an inhibition term, e.g., $P = P_{max}(1 - e^{(-\alpha Eo/Pmax)})$ or: $P = P_{max}(1 - e^{(-\alpha Eo/Pmax)})e^{(-\alpha Eo/\beta max)}$	P is the photosynthesis rate; P_{max} is the maximal rate of photosynthesis; E is the light intensity; α is the initial slope and β is the inhibition slope (Jassby and Platt, 1976; Smith, 1936)
Predator grazing rate	Prey concentration	Ingestion rate Clearance rate	$I = I_{max}[d/(Km + d)]$ $C = C_{max}[Km(Km + d)]$	I is the ingestion rate; I_{max} is the maximal ingestion rate; d is the prey density; Km is the half-saturation for food density C is the clearance rate; C_{max} is the maximal clearance rate; other symbols as above (Hansen et al., 1997; Holling, 1959)

variable fluorescence, but data are not interchangeable. Whereas ^{14}C measurements determine the rate of incorporation of C, ^{18}O experiments measure the water splitting reaction and non-cyclic electron transport, and variable fluorescence instruments (e.g. FRRF, PAM) measure photochemical efficiency of the photosystem II pathway; these rates are not equivalent nor are the kinetic parameters derived from them (Suggett et al., 2009). This presents a challenge for correctly incorporating kinetic constants in model formations. As another example, some nutrient kinetic measurements are made following depletion of substrate over time, while others are made using stable isotopic techniques and the comparative kinetic parameters derived differ (Harrison et al., 1989). Furthermore, measurements made over different periods of incubation or with different competing substrates have long been known to complicate interpretation of *in situ* rates or uptake kinetics (Dugdale and Wilkerson, 1986; Gandhi et al., 2011). Whereas short term experiments measure uptake, longer scale experiments are skewed towards measurement of assimilation or growth (Wheeler et al., 1982; Goldman and Glibert ,1983, Fig. 2). Different species have vastly different capabilities for taking up nutrients and storing them in excess of their growth capabilities (e.g., Flynn et al., 1999; Goldman and Glibert, 1982). Most parameterizations of rate processes as a function of substrate assume a steady-state condition for the cell. When cells are not in steady-state the relationship between uptake and growth becomes uncoupled (Goldman and Glibert, 1983).

While uptake or transport rates are generally assumed to be constant for a given process because they are enzymatic reactions, there is, in fact, a wide range of variability in uptake kinetics even for a given substrate and species or functional group (reviewed by Litchman et al., 2006). This, too, presents challenges for model applications. For example, the rate of nutrient uptake as a function of external nutrient availability (Michaelis–Menten model) can be highly variable depending on the physiological state of the cells, the time of exposure to the limiting nutrient, and other environmental factors (Lan Smith et al., 2009; Wheeler et al., 1982 and references therein). Uptake rates of a given element are also variable depending on which form is supplied; ammonium (NH_4^+), for example is typically transported into the cell faster than that of nitrate (NO_3^-), but the interaction of the two may lead to inhibition kinetics (Dortch, 1990; Flynn et al., 1999; Lomas and Glibert, 1999a). Differences in nutrient transport also vary with temperature, although not necessarily proportionately. Uptake rates of NO_3^-, for example, may decrease as temperatures increase, whereas NH_4^+ uptake increases and urea uptake rates varying little with increasing temperature (Fan et al., 2003). This is a function of different temperature optima of the respective enzymes associated with transport and assimilation of these substrates. Time of day is also another important factor, as such processes of uptake and assimilation are highly coupled to the light-day cycle. In this regard, rates of NO_3^- uptake by phytoplankton are particularly sensitive to time of day; the enzyme nitrate reductase (NR) is generally at its daily maximum at first light, and thus rates of NO_3^- uptake are generally significantly higher at this time of day (Cochlan and Harrison, 1991; Glibert et al. 1991). While it is “neither practical, not justifiable, to include all these facets of control within a model” (Flynn et al., 1999, p. 361), the challenge for physiologists is to not only describe the variability but to understand the control of this variability with the expectation that an understanding of controls will lead to more robust general models.

2.3. Regulation across the entire curve

Only under conditions of steady-state — a condition rarely achieved in natural environments — is the uptake rate of nutrients equivalent to growth or the rate of photosynthesis equal to growth (Goldman and Glibert, 1983; Kana and Glibert, 1987a,b). Generally, homeostatic mechanisms keep the acquisition of materials and energy in balance with the cellular growth demands and the observation of relatively constrained

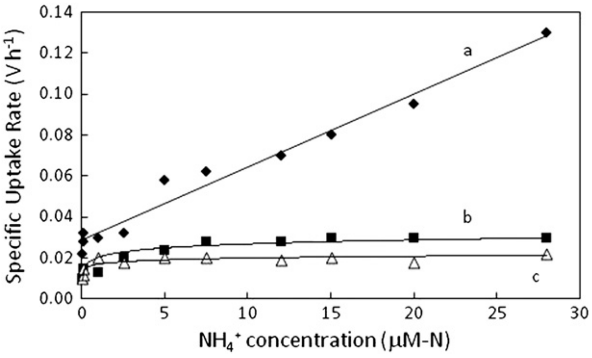

Fig. 2. The specific uptake rate of nitrogen for natural samples from the Chesapeake Bay in which duration of incubation varied (curve a — 1 min; curve b — 15 min; curve c — 60 min). Replotted from Wheeler et al. (1982) with permission of the publisher.

elemental ratios for phytoplankton (e.g., Redfield elemental ratios) is corroborative. However, under non-steady-state conditions relating to variable nutrient or energy availability, cellular adjustments in acquisition efficiency and capacity decouple these 'simple' relationships and the underlying kinetic relationships are always 'chasing' the environmental change. This is part of the general notion that 'physiological state' (the physiological condition as determined by the immediate past history of the cell) can have an important impact on kinetic or energy relationships. A significant challenge is to find tractable ways to tune the parameters of basic kinetic relationships based on physiological states and environmental variability. The evolution of one fruitful approach that was developed in parallel with advances in our understanding of mechanisms of photosynthetic regulation is described below.

The photosynthetic vs. irradiance (PE) relationship is one of the fundamental transfer functions for converting irradiance to photosynthesis. A suite of photosynthesis-irradiance measurements conducted on the marine cyanobacterium *Synechococcus* (strain WH7803) grown across a gradient of irradiances illustrates the large plasticity of the PE relationship depending on growth irradiance (Kana and Glibert, 1987a,b). A classical saturation curve was observed for growth rate with maximal rates occurring above 200 μM photons m^{-2} s^{-1} and up to 2000 μM photons m^{-2} s^{-1}, the highest irradiance tested (Kana and Glibert, 1987a). However, at each steady-state growth irradiance, a unique PE curve was identified (Kana and Glibert, 1987b; Fig. 3). While the rate of photosynthesis measured at the growth irradiance balanced the demand for growth, the overall shapes of the PE curves for cells growing at the different irradiances were significantly different. The different PE curves were a consequence of photoacclimation of photosynthetic pigmentation. At irradiances that saturated growth rate, the cells produced only enough pigmentation to satisfy the energy demands for growth (i.e. the initial slope, α, in per cell or per C units was adjusted to yield a photosynthetic rate that matched the growth demand). Over irradiances that limited growth rate, α increased with diminishing irradiance, but not sufficiently to maintain photosynthesis at a rate that could support maximum growth rate. In those experiments, the maximum photosynthesis rate, P_{max}, identified from the PE curve, exceeded the operational photosynthetic rate in the range of growth limiting irradiances, implying that regulation of photosynthetic capacity (analogous to V_{max}) was not matched to the 'needs' of the cell.

These data exemplify the fact that a generalized saturation curve is characteristic of phytoplankton photosynthesis in that there must be a proportional region (initial slope) and a saturation region (both a consequence of fundamental constraints of the biophysics and biochemistry of photosynthesis), but that the curves are continuously variable within the bounds of the extremes of growth irradiance. In other words, a single PE curve cannot be used to describe a species' photosynthetic activity. More useful, however, is the observation that the derived parameters (α and P_{max}) can be described by simpler relationships to irradiance and that these parameter ranges exhibit species specificity (MacIntyre et al., 2004) providing species-specific information for models. Such data alone, however, would be relatively cumbersome when applied to ecological models, and such descriptions are limited to irradiance as the only forcing function.

Early work on photoacclimation (originally termed photoadaptation), which is ubiquitous among plants and algae, was in the context of "sun vs. shade" or "high vs. low" irradiance acclimation. In that experimental context, species appeared to sort themselves out in terms of two or more 'strategies' depending on patterns of change in α and/or P_{max} (Prézelin, 1981; Richardson et al., 1983), but the *Synechococcus* light gradient study (Kana and Glibert, 1987b) demonstrated that all of the strategies previously described existed in one organism when observed over a growth irradiance range that encompassed limiting and saturating irradiances. This implied a single mechanism for photoacclimation. Subsequently, it was demonstrated that the 'light meter' for photoacclimation resided in the electron transport chain and was related to the reduction state of plastoquinone (Escoubas et al., 1995; Maxwell et al., 1995) whereby a shift in reduction state caused a shift in pigment-protein synthesis rate. The reduction state was shown to be directly related to the *relative* rates of reductant formation via light harvesting and reductant utilization via (principally) carbon assimilation. Thus, an increase in irradiance at constant utilization (e.g., at P_{max}) increases the redox state and reduces the pigmentation which ultimately reduces the redox state to a new poise. This dynamic balance is one of several mechanisms that balance energy absorption with energy utilization, but it is the key mechanism for modelers of phytoplankton productivity because it relates pigment cellular concentrations to the environment.

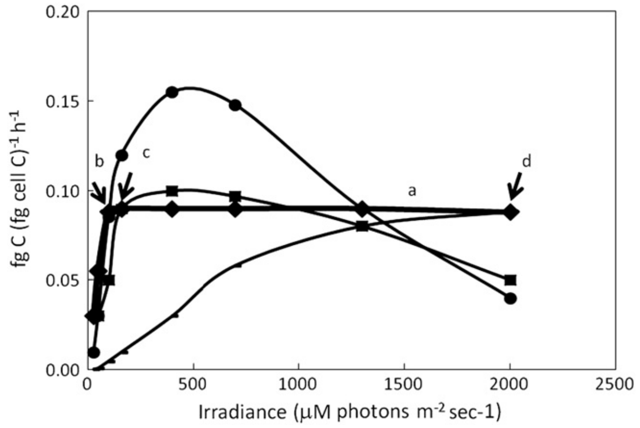

Fig. 3. The relationships between growth rate and photosynthetic response rate (both expressed as fg C (fg cell C)$^{-1}$ h^{-1}) of *Synechococcus* WH7803 as a function of irradiance. The curve indicated by (a) represents the steady-state growth response of cultures pre-adapted to the growth irradiance; curves indicated by (b), (c), and (d) represent photosynthesis–irradiance relationships for cultures pre-adapted to the light intensity indicated and then exposed to the light gradient. Replotted from Kana and Glibert (1987b) with permission of the publisher.

From a modeling perspective, Geider et al. (1996, 1997, 1998) and Kana et al. (1997) were first to apply these principals of photoacclimation and introduced a method for combining the effects of irradiance, temperature and nutrient supply on the photoacclimative state of microalgae based on the dynamic balance of energy flow through the entire photosynthetic apparatus and cell, rather than considering photoacclimation as simply a response to absolute irradiance. The critical point is that photosynthetic stress and/or energy poise is as much related to the ability of the cell to utilize the energy as it is the availability of energy at photosystem II (PSII). The modeling applications are that cellular pigmentation (photoacclimation state) can be driven by the ratio of light absorption (a function of pigmentation concentration) to assimilation (constrained by $P_{max;}$ Kana et al., 1997). Whereas prior growth and photosynthesis models of microalgae provided good mass balance, they generally required prior knowledge of the response of photoacclimation (i.e., a catalog of PE curves or pigment concentrations) in order to define the system. The use of this regulatory term (ratio) eliminated that empirical requirement and provided a 'self-regulating' feed-back formulation for determining photoacclimation state.

Recognizing the importance of assimilation in the control of photoacclimation led to a rationale for incorporating environmental factors other than irradiance in a general photoacclimation model (Geider et al., 1997; Kana et al., 1997). The most obvious environmental factors that would affect assimilation were temperature and nutrient availability, in that temperature has a known influence on enzymatic rate processes and nutrient availability was known to be able to set the growth rate of phytoplankton and hence the utilization of photosynthate. Moreover, there was ample evidence of photosynthetic pigment changes under different temperature and nutrient regimes, although there was no cohesive theory to relate those changes to 'photoacclimation'. To a good first order description, the combination of the regulatory term, and assumptions of nutrient utilization and temperature effects and the species specific parameterization of the models, it was demonstrated that all phytoplankton species are similar in that they regulate their pigmentation around the hinge point of the growth-saturating irradiance that matches assimilation capacity (Geider et al., 1997; Kana et al., 1997).

A similar conceptual approach, undertaken by Ågren (1988), explored the relationships between elemental composition and growth rate of *Micromonas lutheri* and a highly contrasting autotroph, the tree, *Betula pendula*. When scaled to their respective optimal nutrient content (limiting nutrient) and growth rate, the relationships between nutrient content and growth were remarkably similar. Both species regulated their elemental composition similarly with regard to their relative growth rates. In both cases, when rapidly growing they were nutrient rich (low C:nutrient), and when growing more slowly, they were comparatively nutrient poor (elevated C: nutrient).

A number of lessons come out of these examples. One is that if there is a focus on characterizing species diversity and identifying differences among species there is a risk of not identifying fundamental regulatory structures that universally embrace all species. Data on diversity, however, is critical and a precursor as it feeds the analysis of regulatory structures. Another lesson well recognized by modelers is that metabolic details are not always necessary in formulations and that adequate, but robust results pertaining to complex multifactor systems can be obtained by 'stepping back'. Whereas the devil is in the details and that is often where vigorous debates originate, and where interest in species, or functional group differences may lie, vis à vis regulatory control, those details may not be where the important advances are made in modeling complex ecosystems. Lastly, the photoacclimation model originated from a physiological perspective with a basis in photosynthetic regulation. There is a long tradition of phytoplankton models being based on 'physiology' though the temptation is often to take a deterministic approach that combines suites of response curves. Kinetic relationships are dynamic in biological systems and formulations that describe the biology of those dynamics rather than relying on 'calibration curves' should lead to greater insight into the behavior of phytoplankton and greater efficiency in computation. This is a challenge for both modelers and physiologists. Following from this insight into photosynthetic dynamic regulation, a number of dynamic model approaches for physiology are being developed and applied (e.g., Jacob et al., 2007; Lan Smith et al., 2009; Pahlow, 2005; Ross and Geider, 2009).

As with irradiance, regulation of nutrient uptake also does not cease in cells exposed to growth-saturating nutrient concentrations. Because of the perpetual focus on the role of "limiting substrates", the potential for regulation of processes at high concentrations has been significantly understudied. Inhibition of nutrient uptake at high concentrations has been recognized for decades (e.g., Gotham and Rhee, 1981) but has been virtually ignored in nutrient kinetics, unlike its counterpart in photosynthesis physiology, photoinhibition. Alternatively, non-saturable kinetics are observed. This is illustrated by NO_3^- uptake, which at saturating to supersaturating concentrations, does not follow a classic saturating hyperbolic relationship in many algal species (Collos et al., 1992, 1997; Lomas and Glibert, 1999b; Watt et al., 1992). In this region of the kinetic curve, uptake may be linear or biphasic (up to concentrations of ~300 μM-N), with the first transition point occurring at ~60 μM-N (Fig. 4). Nonsaturable kinetics likely involve a diffusion-controlled transfer into the cell (Neame and Richards, 1972). Falkowski (1975) has shown for several diatoms that the cell membrane-associated active carrier transporter for NO_3^- is very efficient (Km, ~1 μM-N) but does saturate, and therefore diffusion may well be an important process contributing to nonsaturating NO_3^- uptake kinetics at high substrate concentrations. Biphasic kinetic uptake of NO_3^- appears to be more prevalent in cool waters and it has been hypothesized that cells (especially diatoms) may take up and store NO_3^- at high intracellular concentrations and use this NO_3^- as an oxidant to dissipate the periodic overflow of electron energy through the activity of NR. At low temperatures, while carbon uptake and metabolism may be limited by temperature and unable to buffer sudden changes in the flow of electrons from the light reactions (particularly on sudden changes in light and/or temperature), NO_3^- uptake and reduction should remain high, allowing for dissipation of these electrons. Therefore, NO_3^- reduction may be characterized as a "futile cycle" for at least those species known to display such non-saturable kinetics (Lomas and Glibert, 1999b). The overall point to be emphasized is that physiological regulation can and does occur across the entire spectrum of substrate conditions and classic kinetic curves do not capture the extent of physiological regulation at substrate super-saturation.

One approach that is showing promise in capturing dynamic regulation of nutrient kinetics is that of optimal kinetics (Aksnes and Egge, 1991; Lan Smith et al., 2009). This approach recognizes that the ability of the cell to up- or down –regulate nutrient uptake is a function of the potential maximum uptake sites, internal enzymes and rates of assimilation. Instead of a half-saturation constant, this approach calculates an affinity uptake rate:

$$V_{aff} = [(V_{max}S)/((V_{max}/A) + S) \tag{2}$$

wherein the relationship substitutes the more classic half-saturation constant (Ks) with an affinity constant, V_{max}/A. In such a formulation, both the affinity and V_{max} may vary with cellular physiology. Thus, as with the photosynthetic "regulatory term", here, too, a ratio provides a more robust measure of the relative abilities of all species to compete for nutrients (Lan Smith et al., 2009). In essence, optimal kinetics assumes that the cells dynamically balance the efficiency of nutrient acquisition at the cell surface and the maximal rate at which these nutrients can be assimilated within the cell, a balance between surface uptake sites and internal enzymes (Lan Smith et al., 2009).

Although nontraditional kinetic relationship modeling has lagged, there have been numerous advances in multi-nutrient kinetic modeling. As an example, Klausmeier et al. (2007) developed a multi-nutrient Droop model to illustrate the dynamics of adaptation of uptake rates over time.

2.4. Emergent properties in response to dynamic balance

Conceptualizing the relationships between physiological processes and growth as a dynamic balance between uptake, assimilative, and dissipatory processes has further implications for cell properties. Emergent properties of cells in response to this dynamic balance include the relative proportions of ribosomes, enzyme activities, gene regulation, cellular pigmentation complement, and ultimately the cell elemental composition. Thus, properties such as chlorophyll:carbon (Chl:C), C:N, N:P or other elemental properties are highly dynamic with growth rate and substrate. The *Synechococcus* example above (Kana and Glibert, 1987a,b) further illustrates the dynamic regulation of cell composition. Across the irradiance range for growth, Chl:C and C:N ratios were highly variable (Fig. 5). Most of the variability was in the light-saturated range for growth, reflecting down-regulation of the pigment complement at high irradiance. In another example of dynamic cell regulation, the diatom *Thalassiosira pseudonanna,* when grown under growth-saturating conditions for light and nutrients, was found to display >2-fold difference in C, leading to variable C:N and Chl:C ratios as a function of saturating, but variable, NO_3^- (Fig. 6). Most of the variation in cellular composition was in the nutrient-saturated region of the curve (>50 μM-N) again reflecting the role of down-regulation at saturation. While flexibility in N:P or C:P in phytoplankton have long been shown in culture experiments (e.g., Finkel et al., 2010; Goldman et al., 1979; Leonardos and Geider, 2004a,b; Quigg et al., 2003; Rhee, 1978), the emphasis in previous experiments has largely been on the effect of nutrient limitation. Variability

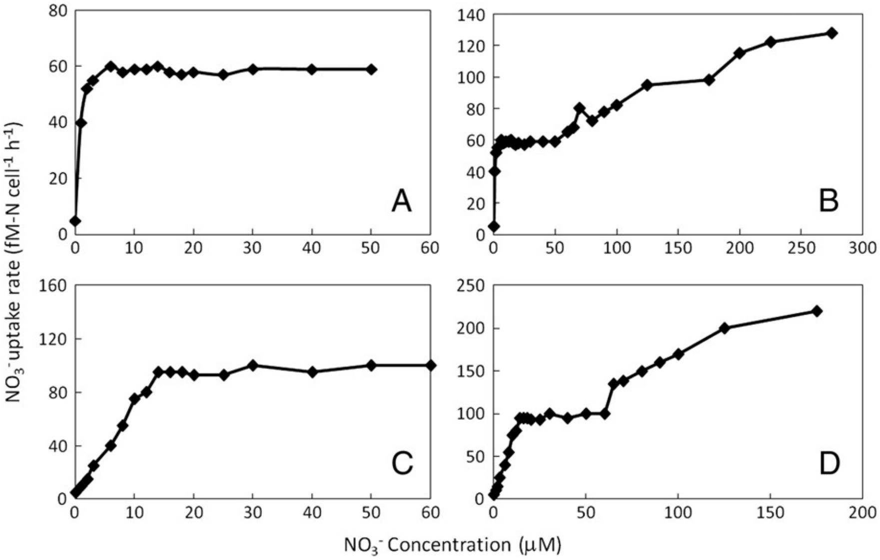

Fig. 4. Examples of biphasic relationships between ambient concentrations of nitrate and specific uptake rate. Panels A and B are for cultures of *Skeletonema costatum*; C and D are for cultures of *Prorocentrum minimum*. Panels A and C illustrate the relationship for concentrations <60 μM; panels B and C illustrate the relationship when the concentration gradient is increased. Replotted from Lomas and Glibert (2000) with permission of the publisher.

in elemental stoichiometry is thus not strictly a response to substrate limitation.

The Geider et al. (1998) model explicitly includes down-regulation of pigment content at high irradiance and(or) when growth rate is limited by nutrient availability or temperature (Falkowski and LaRoche, 1991; Geider et al., 1996); the accumulation of energy-storage polymers when growth rate is light saturated and(or) nutrient limited, as well as the subsequent mobilization of these polymers when light is limiting or nutrients are resupplied (Foy and Smith, 1980); and it includes feedback between N and C metabolism. Dynamic balance models such as those of Kana et al. (1997) or Geider et al. (1998) and many derivatives have advanced the application of multiple currency considerations for phytoplankton growth and take into account the interdependencies of the energy, C, and N metabolism of phytoplankton. These types of models also predict the time course of changes in chemical composition and growth rate that occur when environmental conditions change. In an effort to relate cellular physiological regulation to functional traits across species, a three-way model of the trade-off between cell size and competitive abilities for N and P in marine and freshwater phytoplankton was recently developed (Edwards et al., 2011).

3. Dynamic regulation and ecological stoichiometry

Kinetic models (including photosynthesis models) are fundamentally rate-based models and such structure is essential for describing dynamic processes. Nevertheless, food webs are not merely summations of a series of rate processes (and kinetic curves), but are an outcome of both the quantity and quality of the substrate (or food) provided, not just the rate at which it is produced. The ecophysiology (nutritional quality) of the component organisms present in the ecosystem affects not only their own growth potential but also the activities of others: the cellular composition of algae, for instance, has consequences for grazers. Thus, for grazers, the nutritional value of the prey, not the rate at which it is produced is a key aspect of their population success. From the population standpoint, however, rate of growth of the prey population is important. Therefore robust foodweb/ecosystem models should incorporate not only kinetic parameterization, but also sufficient description of material composition that relates to nutrition. Toward this end, there have been significant advances in our understanding of how essential elements and chemicals structure foodwebs.

3.1. Dynamic nutrient regulation at the producer vs. consumer level

The relative balance of nutrients affects all aspects of behavior of their consumers, such as growth rate, fecundity, and ultimately the success of different populations (Jeyasingh and Weider, 2005, 2007). Compensatory feeding can also occur when grazers are provided food of poor nutritional composition (e.g., Augustin and Boersma, 2006). Classic ingestion relationships emphasizing food quantity (Table 1), not quality,

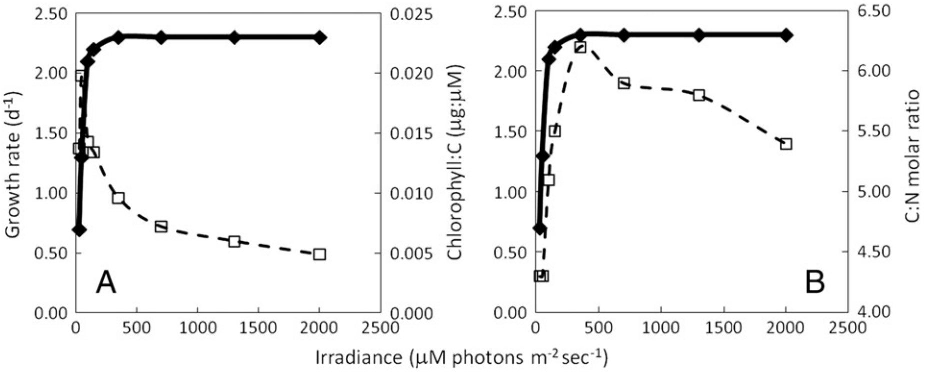

Fig. 5. Comparison of the growth–irradiance relationship (solid line, left axis) and the cellular composition (dashed line, right axis) of *Synechococcus* WH7803 when pre-adapted to the irradiance indicated on the X-axis. Panel A, Chl:C ratio and growth; panel B, C:N ratios and growth. Data derived from Kana and Glibert (1987b).

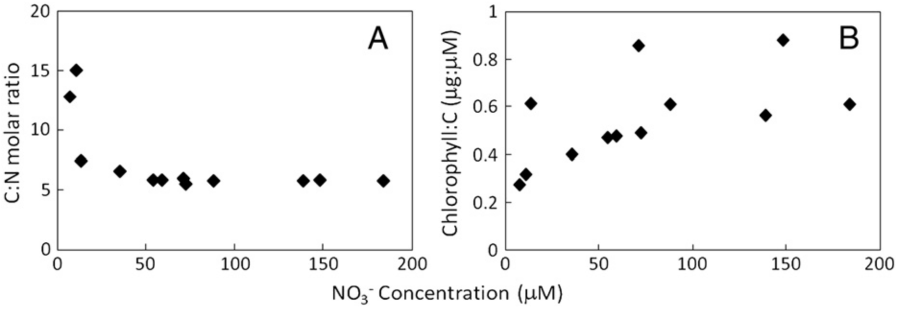

Fig. 6. Comparison of the cellular composition of *Thalassiosira pseudonanna* as a function of nitrate concentrations in the media when grown in turdibistat culture at growth saturating light intensity, and at nutrient concentrations normally taken to be saturating for growth. Panel A illustrates the ratio of C:N, and panel B the ratio of chlorophyll:C.

do not take this into account. Ecological stoichiometry (sensu Sterner and Elser, 2002) provides "an integrated framework for merging perspectives across individual, population, community, and ecosystem levels "(McIntyre and Flecker, 2010, p. 539). In essence, a stoichiometry approach applies the "curve for all reasons" by "imagin[ing] both consumer and prey not as organisms but as amalgams of numerous chemical elements. Prey serve as the reactants …and the consumer's tissues are a product…" (McIntyre and Flecker, 2010, p. 540).

Using the same *Synechococcus* example described above (Fig. 5), all other conditions being equal, it can be inferred that grazers consuming cells growing at 300 μM m^{-2} s^{-1} will gain more C relative to N than those grazing *Synechococcus* growing at 2000 μE m^{-2} s^{-1}, even though the cyanobacteria are growing at the same, maximal rate under nutrient replete conditions. Similarly, grazers consuming *T. pseudonnana* growing at a NO_3^- concentration of 50 μM-N will acquire about twice the cellular N compared to grazers consuming those diatoms growing at a NO_3^- concentration of 150 μM-N (not unheard of for eutrophic conditions), even though in both cases, the NO_3^- was in excess of classic kinetic considerations (Fig. 6).

An important question for ecosystem dynamics, and ultimately for modelers, is the extent to which elemental stoichiometery alters food webs. Grazers and producers operate in a dynamic balance with respect to nutrient composition and availability (Glibert, 1998). Grazers release nutrients directly, but they also consume producers which are the primary consumers of nutrients, and other grazers, which are also nutrient regenerators. Preferential grazing on different predators will affect the flow of regenerated nutrients. Grazers are thus affected by food quality and they, in turn, affect food quality by altering the composition of nutrients available to them.

While individual nutrients, light availability, and cellular nutrient ratios regulate the *growth* of phytoplankton, the wide plasticity of cell composition in algae under both nutrient limited and nutrient-saturated conditions alters the elemental *quality* of the algal food available to grazers. In other words, while primary production can constrain secondary production, N and P availability to the phytoplankton can regulate the types of organisms found in the upper trophic levels via effects of elemental composition at the primary producer level (Glibert et al., 2011). As noted by Sterner and George (2000, p. 127), "Nutrient flux from resources to consumers and then to waste products can be thought of as a chemical reaction wherein *mass must balance*" (emphasis added). Moreover, as noted by Malzahn et al. (2007, p. 2063) based on Brett (1993), "stoichiometric needs of secondary consumers and the stoichiometry of prey are normally finely tuned." Thus, grazers, like algae, are continually challenged with maintaining their nutrient and energy balance.

However, unlike algae, which generally have wide plasticity in their C:N:P stoichiometry (but see Hall et al., 2005), grazers are generally more constrained in stoichiometry; there is typically a mismatch between the stoichiometry of grazers and their food (Sterner and Elser, 2002). Grazers are able to stabilize their biomass stoichiometry more than phototrophs because they have more dissipatory pathways (release and excretion) to eliminate nutrients acquired in excess (Sterner and Elser, 2002). The relationship between stoichiometry of resource or prey and that of the consumer can be related conceptually. Grazers may 1) reflect the stoichiometry of their prey (within reasonable limits), 2) be more restrictive in their stoichiometry than their prey, or 3) be highly constrained in their stoichiometry (Fig. 7; Sterner and Elser, 2002).

Whether grazers are highly constrained or more flexible in their stoichiometry has large consequences for nutrient regeneration, as those grazers that are highly constrained will, by necessity, regenerate the nutrients that are consumed but not needed to maintain their biomass. By regenerating the nutrients not needed, but sequestering those that are needed, positive feedbacks are developed, further accentuating the limiting nutrient and skewing the system toward that in excess (Elser et al., 2000; Sterner and Elser, 2002). For example, in principle, grazers with strict stoichiometry feeding on phytoplankton that are N-rich will excrete proportionately more N than those grazing on phytoplankton that are more balanced in their N:P or N:C ratio. By excreting more N, the condition of excess N is maintained for the phytoplankton (Sterner and Elser, 2002). Such a condition creates wide variations in the stoichiometry of producers and consumers, and presents further cellular challenges for producers to regulate both the limiting and saturating nutrient cellular levels. There are, as yet, no dynamic models that fully capture the positive and negative feedbacks of variable producer and consumer stoichiometry. However, Grover (2002, 2003, 2004), in models of predator–prey interaction involving several prey and one predator with three essential elements, has taken a dynamic balance approach and has illustrated that the long-term outcomes of competition, predation and nutrient cycling are complex but are fundamentally governed by the balance between assimilation and recycling of nutrients, i.e., the extent to which predators sequester or recycle their nutrients. Ramin et al. (2012) also recently developed a complex biogeochemical model of multiple chemical elements (C,N,P, Si and O), and multiple primary and secondary producer functional groups to address the interaction of nutrient regeneration on plankton food webs. They highlighted the interaction between nutrients, the recycling of nutrients, trophic state and the physical structure of lake ecosystems.

An ecological stoichiometric approach is based on the transfer of elements, N and P, as well as C and other elements through the food web, rather than on the rate of production of organic C. Improving the empirical basis for modeling variable stoichiometry and its effects through the food web requires recognition that phytoplankton stoichiometry is not a fixed proportion and that it varies as a function of both nutrient limitation and nutrient saturation. In ecological stoichiometric terms, r-strategists generally have a low N:P ratio and have a higher proportion of growth machinery (ribosomal RNA; high P), whereas K strategists have a higher N:P ratio and have more resource acquisition machinery (enzymes and proteins; high

N; Elser et al., 2000; Klausmeier et al., 2004; Arrigo, 2005; Elser, 2006; Finkel et al., 2010). Organisms that either feed on, or preferentially sequester P from P-sufficient diets will have a higher P body content and can, themselves sustain higher growth rates (more RNA), or may have more P-containing structural components (skeleton and bone) (Elser et al., 1996; Sterner and Elser, 2002). The extent to which primary producers vary in their nutritional content across the entire spectrum of substrate availability is considered to be a major food quality- and food web structure- regulator.

For grazers, the challenge of acquiring the requisite nutrients and balancing biomass stoichiometry is compounded by several factors and the scale on which the relationship is examined. Stoichiometry affects various life stages of the predator differently (Moe et al., 2005). As a specific example, there is a greater need for C, N, and P for developing copepod juveniles, but at a later stage, while C is still needed for metabolism, more P must be allocated to eggs; thus, P-poor food can disproportionately affect egg production while not affecting survival (Færøvig and Hessen, 2003; Laspoumaderes et al., 2010).

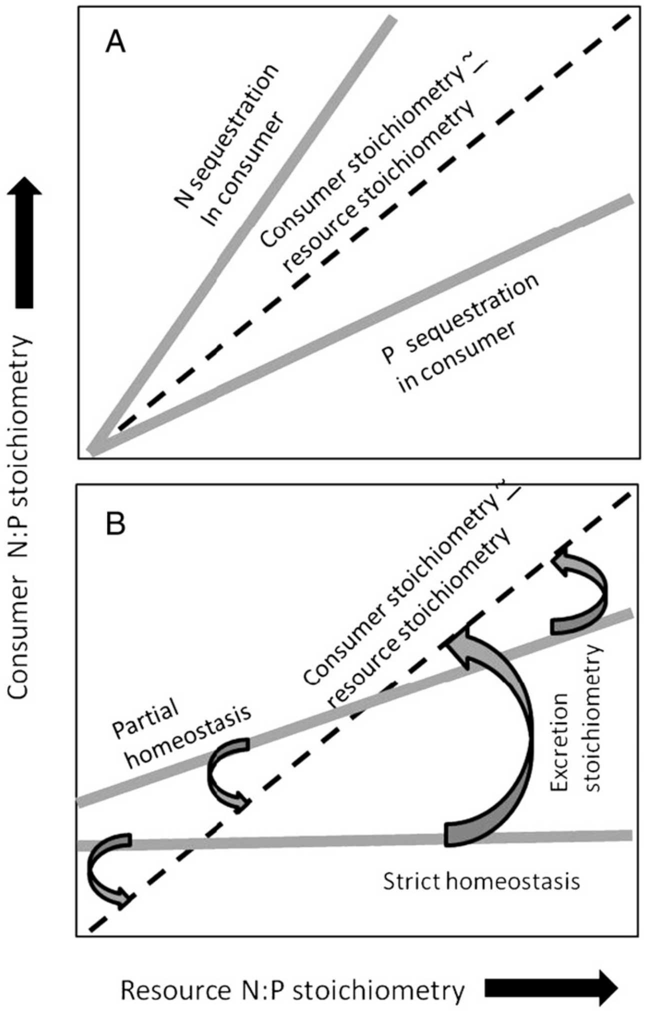

Fig. 7. Schematic relationships between resource N:P (either dissolved nutrients or prey) and consumer N:P. The dashed line in both panels represents the hypothetical situation in which the consumer N:P matches that of its resource. (A) Hypothetical situations in which the consumer is either N or P enriched relative to its resource in a constant proportion. (B) Hypothetical situations where the consumer either partially or strictly regulates its biomass N:P regardless of the N:P of its resource. The arrows depict the extent to which the excreted or released nutrients differ in N:P from that of the consumer biomass N:P. Excretion N:P is expected to be negatively related to substrate N:P when the consumer N:P is constrained. Reproduced from Glibert et al. (2011) with permission of the publisher.

Thus, just as nutrient uptake and growth (or photosynthesis and growth) can be uncoupled, so too is the case for food ingestion and assimilation by zooplankton. And, as the case for phytoplankton, most models assume a fixed relationship across the prey concentration spectrum when the relationship is highly variable (Flynn, 2010). The complex relationships between food quality, feeding rates, and grazer growth rates on trophic interactions are only beginning to be modeled with any degree of skill (Mitra and Flynn, 2007).

3.2. Food quality beyond stoichiometry

While the relative balance of elemental availability affects all aspects of the grazer's ability to meet its nutritional and reproductive demands, it ultimately may be a necessary but insufficient characterization of food quality. Trophic fitness parameters, such as rate of growth or fecundity, are related to the nutritional composition of the food on which they graze, and thus ultimately food quality affects the transfer of energy and nutrients through the food web (e.g., De Troch et al., 2012). Nutritional quality of the algae may be interpreted in terms of elemental composition in the context of the requirements by grazers for acquisition of particular fatty acids, as a measure of the food quality of algae (e.g., Ågren et al., 1990; Brett and Müller-Navarra, 1997; Coutteau and Sorgeloos, 1997; Weers and Gulati, 1997). Some diatom species, for instance, produce certain highly unsaturated fatty acids that are essential for zooplankton reproduction (reviewed by Kilham et al., 1997) while flagellates generally produce different fatty acids than diatoms (Olsen, 1999). Different types of copepods preferentially graze on algae at different growth stages in order to obtain food of a higher C:N content or different fatty acid composition (De Troch et al., 2012). Moreover, while some heterotrophic protists may alter biochemical components that can improve poor algal quality for subsequent higher trophic levels, trophic "upgrading" by such a phenomenon is also highly species specific at the level of both prey and predator (Klein Bretelet et al., 2004; Tang and Taal, 2005; Tang et al., 2001).

Stoichiometry of the prey can also affect other aspects of food quality, including toxin production, cell membrane thickness, and other chemical constituents that have been considered to turn good food "bad" (Mitra and Flynn, 2005). For example, toxin production by numerous harmful algae has been shown to increase when the cells are not grown under nutrient-balanced conditions and when they sustain a change in N or P availability or depletion (Flynn et al., 1994; Johansson and Granéli, 1999a, 1999b; Granéli and Flynn, 2006). Production of toxins rich in N might be regarded as a dissipatory mechanism of algae, whereby cells acquire the nutrient(s) they need but release nutrients that are not needed (reviewed by Glibert et al., 2011; Glibert and Burkholder, 2011). In some algal flagellates, toxin production increases under P stress (Granéli et al., 1998; John and Flynn, 2002). Toxin production for stoichiometric balance under N limitation appears to be less common than under P limitation, perhaps in part because many toxins are N-rich (Granéli and Flynn, 2006). The dominance of toxin-producing species can result in a failure of normal predator–prey interactions, which, in turn, enhances the transfer of nutrients that sustain HABs at the expense of competing algal species (Irigoien et al., 2005; Mitra and Flynn, 2006; Sunda et al., 2006).

Superimposed on these factors is also the consideration of whether substrate quality or food quality is altered on an episodic basis, or whether changes are long-term and sustained. As conceptualized by Hood and Sterner (2010), a change in predator growth rate to altered diet depends on the extent to which the diet is sustained or switches, with variable frequency, between low-quality food and high-quality food- in this case, defined by the relative P content (Fig. 8). In natural environments, poor quality food such as detritus, may be an important food for many grazers. From a stoichiometric perspective, detritus, high in C, may result in metabolic costs to consumers, including altered metabolic rate and growth rate (Hessen and Anderson, 2008; Plath and Boersma, 2001). Detritivores consume the least nutritionally balanced foods and thus have lower growth rates than their planktivorous or piscivorous counterparts (Sterner and Elser, 2002). Release or dissipation of excess C appears to have major impacts on organismal fitness and, like the other stoichiometric concepts explained above, can affect ecological interactions at the ecosystem level and enhance stoichiometric regulation (Hessen and Anderson, 2008). Vanni (2002), for example, examined the stoichiometry of 28 species of fish and amphibians, and their data suggested that elemental stoichiometric controls were strongest when consumers ingested nutrient-poor items such as nutrient-limited algae or detritus. The effects were weaker when consumers ingested multiple food items including other animals that were apparently more nutrient-rich.

3.3. Organismal demands and community assembly

In spite of all of the complexities noted above as well as others not covered herein, there is a growing recognition that ecological stoichiometry has proven to be a valuable construct at all levels of the food web, but it may be that its value increases with trophic level and long time scales, as higher trophic levels are more stoichiometrically constrained, and reproduction and skeletal investment is a function of nutrient availability rather than energy availability (McIntyre and Flecker, 2010; Sterner and Elser, 2002). However, developing bottom–up, or reductionist, models of large-scale trophodynamic relationships that provide the same outcomes as the conceptual stoichiometric ecological theory is daunting. The observation that annually averaged data (nutrient and biotic) provide good correlative relationships in the context of the ecological stoichiometry theory (Glibert et al., 2011; Smith, 2006) argues that control of such broad patterns involves a significant 'filtering' of seasonal, event scale, diel and physiological scale processes. Conceptually, the 'filtering' may be analogous to phytoplankton assimilative metabolism described above in the example of photoacclimation. In both contexts, the underlying mechanisms adhere to certain higher level constraints (e.g., regulation of material and energy balance) that are quantifiable and understandable. Logically, for ecosystem processes that exhibit relationships to nutrient (element) stoichiometries, mass balancing element flows should be tractable, but it requires identifying the principal agents and getting the kinetics 'right' for those agents. Such an approach is important in that it can be used to identify the 'ecological engineers' from the 'ecological passengers'. [The rigorous ongoing debate about whether chemical changes from physiological assimilation and dissimilation constitutes 'ecological engineering' bears relevance but will not be elaborated here (Wright and Jones, 2006; Byers, 2007; Berke, 2010)]. Importantly, as trophic complexity changes, so too does regulation by stoichiometric control (Leiss et al., 2006; McIntyre and Flecker, 2010).

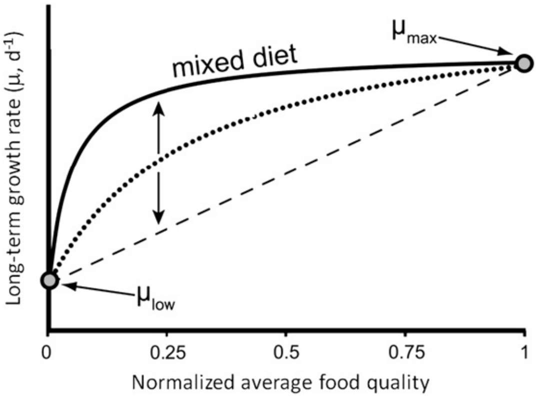

Fig. 8. Conceptual relationships between long-term growth rate of consumers in relation to normalized food quality (expressed as the phosphorus:carbon (P:C) ratio). The dashed line indicates food that is comparatively rich in P; the dotted line indicates food that is comparatively poor in P; the solid line indicates a diet that switches between low and high quality food with variable frequency. With constant, but mixed diet food supply, a saturating response develops between growth of the consumer and food quality. The shape of the curve varies when food is of high or low food quality. Replotted from Hood and Sterner (2010) with permission of the publisher.

Several recent reviews have addressed the stoichiometry of higher aquatic food webs, namely fish (Hendrixson et al., 2007; McIntyre and Flecker, 2010; Sterner and George, 2000). Not only is there a strong shift in body N:P with growth stage (Pilati and Vanni, 2007), but there are also strong phylogenetic contrasts. In fact, Hendrixson et al. (2007) demonstrated, for 20 families of fish, that a phylogenic tree could be developed based on the body P, C:P, and N:P, but not in C or N. For fish, the most important determinant of stoichiometry is structural demand; growth demands appear to be secondary (McIntyre and Flecker, 2010). The variability in diet presents enormous challenges for dynamic regulation of biomass stoichiometry in fish. Diets may vary in C:N from 5 to 75 times that required for growth, and C:P may be up to several orders of magnitude higher, depending on species and environmental conditions (McIntyre and Flecker, 2010). Bioenergetic models coupled with stoichiometric models (e.g., Frost et al., 2006; Hood et al., 2005; Schindler and Eby, 1997) will be required to fully understand the physiological and nutritional regulation at all dietary levels. At all levels of the food web, energy regulation (C flow) and nutrient regulation are fundamentally regulated differently. Where energy flow and elemental cycling have been explicitly examined in a two-trophic level chain population model, for example, dynamical behavior emerges that illustrates that energy enrichment of the system results in very different trophic stability and altered predator–prey interactions than does nutrient enrichment (Loladze et al., 2000). Population models with stoichiometric constraints between predators and prey behave quite differently from those without stoichiometric regulation (Anderson et al., 2004). In a recent analysis of internal regulation of species in relation to external forcings, Klausmeier (2010) developed a predator–prey model illustrating multiple stable annual trajectories and year-to-year irregularity in successional trajectories. Clearly, there are opportunities for advancing these approaches with realistic understanding of dynamic elemental regulation at all levels.

The long-term changes in the food web of the San Francisco Estuary Bay Delta provide an interesting example of how populations at all levels of the food web may self-assemble in relation to long-term nutrient changes via feed-backs with trophic and biogeochemical stoichiometric changes (Glibert et al., 2011). At the phytoplankton level, there has been a loss of diatoms over the past several decades, related to several factors, among them an increase in N:P in the land-based nutrient load and an increase in the relative availability of NH_4^+ in the N pool (Dugdale et al., 2007; Glibert, 2010; Glibert et al., 2010). Diatoms, being generally considered an "r" selected group, would be expected to have a low N:P ratio and thus would be expected to be outcompeted if N:P in the environment increases. In this system, dinoflagellate abundance was positively correlated with N:P ratio over the decadal scale. Dinoflagellates are generally considered a "K" selected algal group. At the zooplankton level, among other changes, there has been a long-term change in the relative abundance of the calanoid *Eurytemora* and the cyclopoid *Limnoithona*. The former has not only declined with time, but the most precipitous change was in the mid 1980s. The latter is considered an invasive species (Kimmerer, 2004), with its population increasing several orders of magnitude since its introduction also in the mid 1980s. Calanoid copepods generally have a high N:P ratio of their biomass, ~20–35 by atoms, whereas cyclopoid copepods have N:P ratios much closer to Redfield atomic ratios (Sterner and Elser, 2002; Walve and Larsson, 1999). The oscillation of the calanoid copepod *Eurytemora* with the cyclopoid copepod *Limnoithona* over time is a near mirror image of the oscillation in the N:P ratio, a pattern consistent with these grazers being responsive to changes in elemental stoichiometry and maintenance of altered dynamic equilibria on a long-term scale

(Fig. 9). Other changes in community composition also have been shown to have paralleled changes in N:P ratio over the decadal scale in this system. Numerous changes in invertebrates and in fish community composition changed in relation to diatoms, and to N:P (Fig. 10; Glibert, 2010; Glibert et al., 2011). Proportionately greater sequestration of P in the biomass of the omnivorous fish would lead to them being proportionately more abundant when P is less available (in the water column). Using the kinetic analogy, proportionately greater sequestration of nutrient is equivalent to a highly efficient uptake strategy. Clearly, changes in nutrient stoichiometry in this system, achieved through both external forces (altered land-based nutrient loads) and internal, organism-driven, assimilative and dissimilative processes, related to community compositional changes (Glibert et al., 2011).

4. Dynamic regulation and biogeochemical cycles

4.1. Oceanic biogeochemistry

Well recognized is the fact that interest in stoichiometric regulation of biogeochemistry has its origin in the seminal Redfield descriptions of elemental nutrient ratios (Redfield, 1934, 1958). Stoichiometric regulation of biogeochemistry recognizes the biotic feedbacks that regulate not only the flow of nutrients and their proportions, but also their effects on ecosystem structure. In simple terms, competition between N-fixing and non-N-fixing phytoplankton regulate this balance along with losses of N due to denitrifiers, and such dynamics have been captured in varying stoichiometry ocean models (e.g., Lenton and Klausmeier, 2007; Tyrell, 1999). It is generally accepted that the biota controls oceanic N:P (Falkowski, 2000; Redfield, 1958). Yet, coupled biogeochemical models typically link biological C production to nutrient fluxes assuming fixed elemental proportions. In the context of climate change the focus of marine ecosystem modeling activity has largely been on C cycling at a global scale (Le Quéré et al., 2005; Moore et al., 2002).

Some advances are being made in considering different elemental pools (including, to greater or lesser extent, C, N, P, Si and Fe) in biogeochemical ocean or global flux models. These models depend on capturing multi-nutrient regulation of different phytoplankton functional groups, including accurate relationships between cell size, sinking rate (export ratios), and other aspects of cell physiology (layered onto the need for accurate three-dimensional physics). The construct of such models is fundamental and the recognition of the role of variable stoichiometry is rapidly advancing. Only a few recent examples are highlighted. Litchman et al. (2006) have developed a multi-nutrient, multi-group model of phytoplankton and applied the model to test various scenarios of future change. They found that the model was not only very sensitive to the kinetic parameters used for the different elements and different functional groups, but that the effect of changing N:P stoichiometry differed for different oceanic regions. Community assembly was sensitive to both levels and ratios of resources. Lan Smith et al. (2009) compared the University of Victory Earth System Climate Model of global climate and biogeochemical cycles when run with standard Michaelis–Menten kinetics and those of the optimal kinetic relationship. Large regional differences in biogeochemistry emerged with the revised kinetic application, including large spatial and temporal differences in primary production. Tagliabue et al. (2011) compared fixed stoichiometric models with ocean biogeochemical models that allowed C, N and P to vary independently and found large variations in net primary production and carbon export in the different models in response to ocean acidification, leading to the conclusion that non-Redfieldian models need to be further developed in ocean-climate applications. Rastetter (2011) recently described the effects of formulating growth of component organisms in a forest ecosystem as a function of classic nutrient limitation or more dynamic regulatory balance and the result was very different predictions of ecosystem function to increased CO_2 and global warming. Using an ocean circulation model, Weber and Deutsch (2010) showed that latitudinal gradients in nutrient

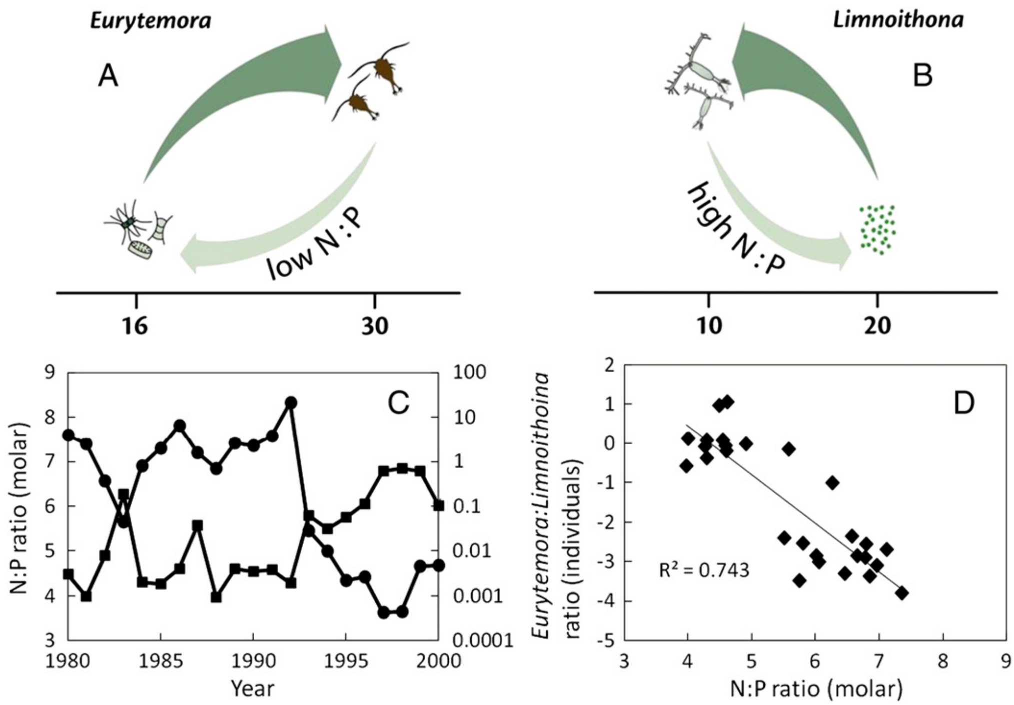

Fig. 9. Conceptual diagram of the ecological stoichiometric relationship between different phytoplankton and zooplankton genera. Panel A represents the relationships between diatoms and the copepod *Eurytemora affinis*; panel B, the relationship between small flagellates and the cyclopoid copepod *Limnoithona tetraspina*. The X axis represents the biomass N:P of the organisms. The wide arrow represents ingestion of the phototrophs by the grazer; the lighter arrow represents nutrient regeneration in the grazer's excretions. Note that the stoichiometry of the regenerated nutrients differs with zooplankton taxon and the N:P ratio of the food on which they graze. Panel C represents the comparison of the ratio of *Eurytemora*/*Limnoithona* and the ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP) for the period from 1980–2000 for Suisun Bay, San Francisco Bay Delta. Panel D is the correlation of the data from (C); the coefficient of determination was significant ($p<0.05$). Panels A and B reproduced from Glibert et al. (2011) with permission of the publisher.

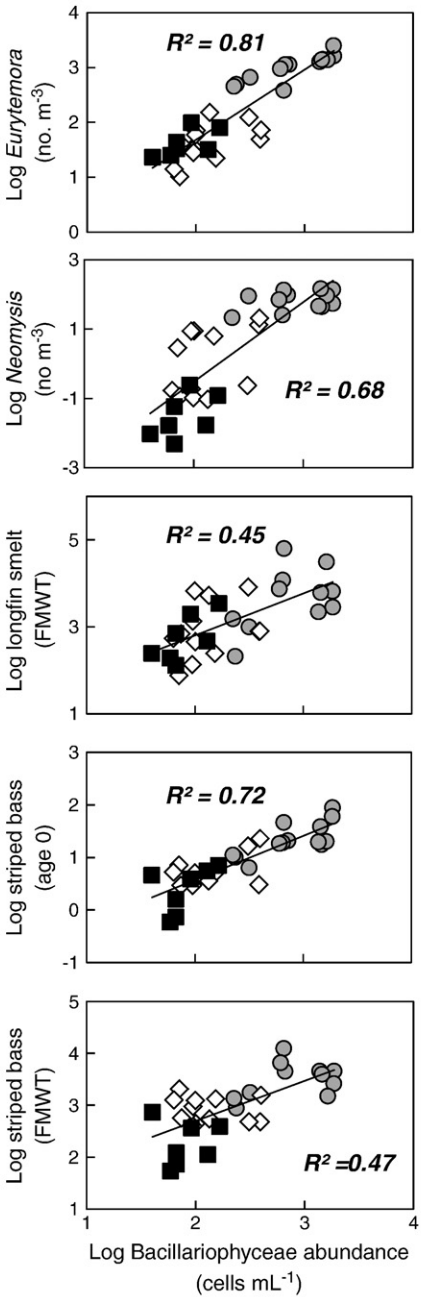

Fig. 10. Comparison of the long-term (1975–2005) change in annually-averaged diatom biomass and that of several other trophic groups for the San Francisco Bay Delta. The coefficients of determination (R^2) were significant ($p<0.05$) in all cases. Data derived from Glibert et al. (2011) from which further information is available on data sources.

stoichiometry were governed by species compositional differences and that (p. 553), "a 25% increase in high-latitude C/P ratios, reflecting an increase in N/P from 16:1 to 20:1, would reduce the concentration of atmospheric CO_2 by ~15% ppm. from interglacial levels." Parameterization of models for the study of global change, and end-to-end trophic dynamics are thus being rapidly developed and implemented, but capturing dynamic behavior, including adaptation to nutrient change will continue to be a challenge.

4.2. Nearshore biogeochemistry

Nearshore biogeochemical processes are well recognized to balance assimilative and dissimilative process and may present even more complex challenges because of the diversity and complexity of sediment exchange processes. Processes such as denitrification, anaerobic ammonium oxidation (anammox), dissimilatory nitrate reduction to ammonia (DNRA) all alter the proportion of fixed N in the system. In the sediment (or in anoxic or hypoxic water columns), remineralization pathways also alter stoichiometry. There are a series of trophic and biotic, as well as abiotic conditions, that may promote fluxes of nutrients in and out of the benthic zone, and transformations of nutrients, altering the stoichiometry for producers. Bioturbation and excretion processes of benthic macrofauna may alter nutrient cycling processes (e.g., Solan et al., 2008). Moreover, colonization of sediments by benthic macrophytes may have both direct and indirect effects on nutrient remineralization and its stoichiometry. Bioturbators may change sediment-nutrient dynamics through sediment mixing and tube or burrow-building; they also alter redox conditions at the sediment–water boundary (Aller, 1994; Kristensen, 2000). Macrophytes take up nutrients from the water column and the sediment, but may also increase the surrounding pH from their high productivity under some conditions. The latter fit the classic definition of 'ecosystem engineers' in that they alter both the biotic and abiotic habitat (Berke, 2010; Jones et al., 1994).

Highly productive nearshore areas affected by high macrophyte productivity alter the pathways by which N and P are cycled in many ways. By their production, pH can be locally elevated, affecting the biogeochemical cycling of N, including the chemistry of NH_4^+-NH_3 and processes such as nitrification, denitrification, and DNRA (e.g., Huesemann et al., 2002; Kemp et al., 2005; Glibert et al., 2011). Both bacterial production and respiration can be negatively affected by alkaline pH resulting from high rates of macrophyte photosynthesis which, in turn, affects C cycling and energy flow and reduces rates of remineralization (Tank et al., 2009). Classic work by Barko and Smart (1980) showed that PO_4^{3-} turnover in the interstitial water increased 1000-fold in sediments supporting Eurasian milfoil or *Egeria dense* growth. As pH increases, the fundamental physical-chemical relationships related to P adsorption–desorption change. Enhancement of sediment P release under elevated water-column pH conditions has been observed in eutrophic lakes (i.e., Drake and Heaney, 1987; Jensen and Andersen, 1992; Xie et al., 2003) and tidal freshwater/oligohaline estuaries (Seitzinger, 1991).

Positive feedback mechanisms thus exist between microbial processes, macrobenthos, macrophytes, pH, nutrient efflux, and other biogeochemical processes affecting stoichiometry, and in turn, food webs. Incorporating the full complexity of these interactions is an enormous challenge for modelers, but there are important steps being made in recognizing these complex interactions. Understanding and parameterizing these important feedbacks not only has implications for modeling current and projected changes in climate, nutrient loads, and land use, but it also has direct application in understanding thresholds of system response or altered stable states (sensu Scheffer et al., 1993).

4.3. Eutrophication and future nutrient change

Eutrophication and nutrient pollution is occurring due to the increase in human population, the increasing demands on energy, increases in nitrogen (N) and phosphorus (P) fertilizer use for agriculture, changes in diet, leading to more meat production and animal waste, and expanding aquaculture industries (e.g., Galloway and Cowling, 2002; Galloway et al., 2002; Glibert et al., 2006, 2010; Howarth, 2008; Howarth et al., 2002; Smil, 2001; Wassmann, 2005). While the effects of eutrophication are well known, such as changes in species diversity, excessive algal growth, reductions in dissolved oxygen, fish kills, and the increased prevalence or frequency of toxic algal blooms, two specific issues with regard to nutrient pollution are relevant here. First, in eutrophied systems, primary producers are often exposed to saturating- or super-saturating nutrient concentrations. Thus, these algae are subject to the kinds of cellular regulatory processes described above and that have consequences at all levels of the food web. A few such responses were described above, but there are many adaptations at growth-saturating or super-saturating substrate levels that have important bearing on production and nutrient transport and ultimately on ecosystem function — photoadaptation, photoinhibition, antioxidant production, toxin production, DMS production, photorespiration, among others. These dissipatory processes are not now captured in assimilatory model constructs of phytoplankton metabolism and present additional opportunities for advancement.

Second, anthropogenic nutrient loads are not in classic stoichiometric proportion — or are rapidly changing — and thus external drivers may have effects and feedbacks on nutrient availability that are complex at all levels. Of potentially large importance for ecosystem structure is the enhanced enrichment of the globe with N relative to P (e.g., Galloway and Cowling, 2002; Galloway et al., 2002; Glibert et al., 2006, 2010; Howarth, 2008; Howarth et al., 2002; Smil, 2001; Wassmann, 2005). It has been estimated that the atmospheric deposition of nutrients in the ocean is now ~20 times the Redfield ratio for N:P (Jickells, 2006; Peñuelas et al., 2012) and is having large consequences for N:P stoichiometry in lakes (Elser et al., 2009). Global use of N has increased relative to that of P, especially since the mid 1990s (Fig. 11). Aggressive removal of P loads relative to N — for example, from sewage effluent and laundry detergents — is also accelerating this change (e.g., Litke, 1999). These changes are thought to be affecting biodiversity from land to the sea, beginning at the level of the N content at the genome and proteome level (Acquisti et al., 2009; Peñuelas et al., 2012).

In typical eutrophic conditions the minimum configuration of multiple currency models should consider C:N:P. Many systems will also require inclusion of Si, and some may require inclusion of Fe. Variable elemental stoichiometric models should become the norm. Multi-element descriptions, as opposed to fixed Redfield constructs, provide a basis for the development of mechanistic models that contain functional response descriptors with recognized physiological bases (Flynn, 2010; Glibert et al., 2010). Multi-element descriptions also support bioenergetic descriptions, which may be important for predicting the survival of organisms under unfavorable conditions. Variable stoichiometric parameterizations in models must also begin to recognize that physiological processes and organismal stoichiometry can and does vary even at growth-saturating substrate concentrations.

5. Implications, challenges and future opportunities

Varying biomass stoichiometry has enormous ramifications for affecting organismal traits and ultimately trophic transfer. They, in turn, affect biogeochemistry — and are affected by — those changes. The efforts to incorporate dynamic balance models for physiology and for trophodynamics need to be advanced. The plasticity of nutritional pathways, as well as the plasticity of food web interactions, including grazing, allelopathy, symbioses and other interactions, creates immense challenges for model constructs. Monod and Michaelis–Menten kinetics which assume a fixed half-saturation constant and maximal rate are inadequate, and in many (most?) cases incorrect, to capture variable physiological processes. Even cellular Droop kinetic relationships do not classically capture regulation beyond saturation. A new generation of models is needed to capture stress at the supersaturating end of the spectrum as well as at the limiting end; the dynamic equilibria (Allen and Polimene, 2011; Flynn, 2010). As noted by Allen and Polimene (2011), it is time to conduct the experimental work required at all scales that will "fully capture ecosystem dynamics…the physiology of the component organism, their behavioral traits and the interactions between them." As described above from the lessons of photosynthetic regulation, it is both the fundamental regulatory structures that universally embrace all species that need further elucidation, but also critical are data on diversity as they feed the analysis of regulatory structures.

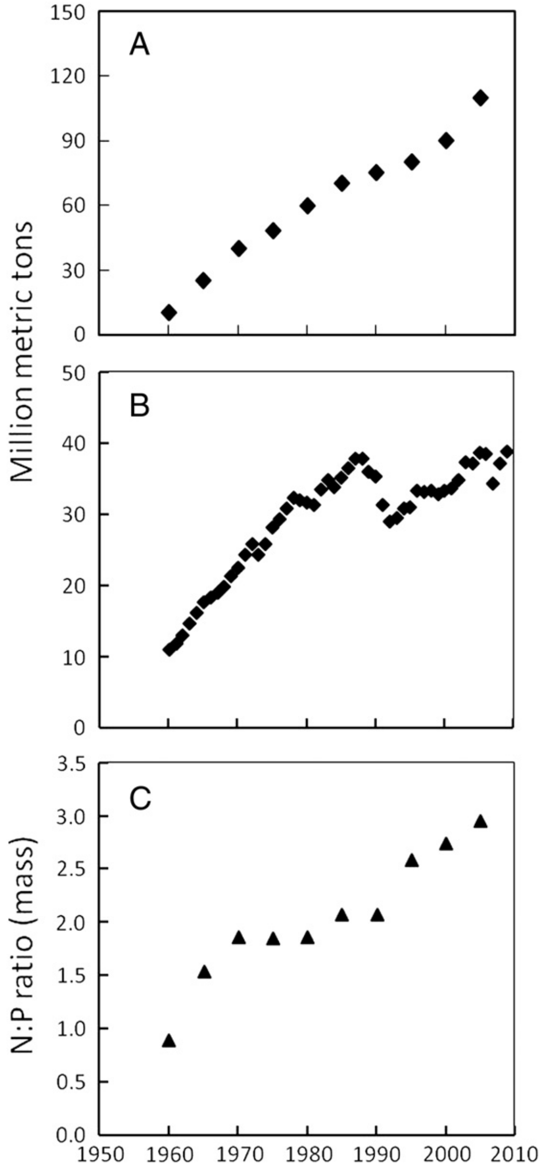

Fig. 11. Comparison of the global change in fertilizer nitrogen (panel A) and phosphorus (panel B) use and the resulting N:P stoichiometric change (panel C) from 1960 to 2010. Data are from the World Fertilizer Institute (www.fertilizer.org; IFIA, 2011).

Models are dependent on data, and at the physiological scale there is a much to be done. More work is needed at the "stress scale", including substrate saturation as a "stress". With the expansion of eutrophication, many coastal, estuarine and freshwater systems now have nutrient loads and concentrations that well exceed those of "saturation" and can be thought of as "super-saturating". Similarly, efforts to control or regulate nutrients are leading to nutrient loads with highly altered stoichiometry. Yet, with the exception of the types of examples provided above, there is little data on substrate uptake at the supersaturating level or its consequence on cellular metabolism and stoichiometry. There is much work to be done to understand physiological trade-offs at varying substrate (both nutrients and light) across functional groups, parameterizing rates, characterizing traits, and how they are both externally driven and internally dynamically regulated. Without question, "model solutions are dependent on choices made for implementation approaches and parameterizations that arise because of the scales that are addressed by the model…and improvements in simulation of phytoplankton distribution and production will require inclusion of more than one functional group" (Hofmann et al., 2011, p. 114, 115).

It is time to lay to rest the notion that nutrients and nutrient stoichiometry are only regulatory for physiology at the limiting end of the spectrum. It is time to dispel the notion that high energy input (C flow) is all that is required for a highly productive ecosystem. The increasing nutrient loads to coastal systems, combined with their disproportionate composition in both space and time make the issue of stoichiometry ever more important (Glibert et al., 2006; Howarth et al., 2005; Seitzinger et al., 2002, 2005). Disproportionate N and P loads globally are now recognized to have effects at all scales, from genomic to ecosystem that need further empirical resolution (Peñuelas et al., 2012). Even relatively small changes in nutrient supply are being shown to have large consequences on many important properties of the ecosystems (Nielsen, 2003). Understanding the full suite of processes and factors that underlie variable stoichiometry at all scales — and for elements beyond N and P emphasized here — and the feedbacks between them is a grand challenge (Frigstad et al., 2011). Imbalances in stoichiometry not only have consequences for trophic transfer and biogeochemistry as described here, but can and will change patterns of sequestration of C and many other processes of the structure and function of ecosystems. Climate change, altered CO_2 levels, and their implications for altered productivity of a global ocean should motivate both new dynamic balance model architectures and new experimental investigations that support them.

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Elevated ammonium concentrations from wastewater discharge depress primary productivity in the Sacramento River and the Northern San Francisco Estuary

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ABSTRACT

Primary production in the Northern San Francisco Estuary (SFE) has been declining despite heavy loading of anthropogenic nutrients. The inorganic nitrogen (N) loading comes primarily from municipal wastewater treatment plant (WTP) discharge as ammonium (NH_4). This study investigated the consequences for river and estuarine phytoplankton of the daily discharge of 15 metric tons NH_4–N into the Sacramento River that feeds the SFE. Consistent patterns of nutrients and phytoplankton responses were observed during two 150-km transects made in spring 2009. Phytoplankton N productivity shifted from NO_3 use upstream of the WTP to productivity based entirely upon NH_4 downstream. Phytoplankton NH_4 uptake declined downstream of the WTP as NH_4 concentrations increased, suggesting NH_4 inhibition. The reduced total N uptake downstream of the WTP was accompanied by a 60% decline in primary production. These findings indicate that increased anthropogenic NH_4 may decrease estuarine primary production and increase export of NH_4 to the coastal ocean.

1. Introduction

Nutrient loading is increasing globally due to population growth and intensification of agriculture. Cultural eutrophication and the loading of aquatic systems with nitrogen (N) and phosphorus (P) have long been recognized as important drivers of ecosystem change. Generally, eutrophication is thought to degrade food webs and lead to increases in autotrophic biomass, including nuisance algal species, inefficient trophic transfer, stimulation of microbial activity and hypoxia. However, study of estuarine eutrophication globally for more than three decades has revealed a range of ecosystem responses to nutrient enrichment (Sharp, 2001). Increased nutrients may lead to eutrophication with undesirable consequences, but not in all cases (Cloern, 2001; Sharp et al., 2009). Rather than stimulating algal processes, negative effects on phytoplankton physiology have been observed (MacIsaac et al., 1979; Wilkerson et al., 2006). Reduction in primary productivity associated with anthropogenic ammonium (NH_4) loading has been reported, for example in the Delaware Estuary (Yoshiyama and Sharp, 2006) and a wastewater-dominated Canadian river (Waiser et al., 2011). The San Francisco Estuary (SFE) has also experienced declining primary productivity (Jassby et al., 2002) while receiving increased nutrient loading (Jassby, 2008). It is the largest estuary on the west coast of the US and highly impacted by the urban centers of the San Francisco Bay Area (San Francisco, Oakland and San Jose) and the City of Sacramento and receives nutrient inputs from more than 80 municipal wastewater treatment plants (WTPs) with varying levels of effluent treatment.

Increased loading of NH_4 to the SFE is largely the product of the Clean Water Act requiring the conversion of WTP's to secondary treatment resulting in discharge of N as NH_4. With the exception of Stockton, major cities in the Northern SFE and Delta do not carry out advanced secondary treatment and discharge N primarily in the form of NH_4 rather than NO_3. As of 2006, 75% of the effluent released by Delta treatment plants was processed only to the secondary level (Brooks et al., 2011). Approximately 90% of the total N in the Northern SFE originates from a single point source, at the Sacramento Regional WTP (SRWTP), which discharges approximately 15 metric tons of N per day, largely as NH_4, to the Sacramento River (Jassby, 2008).

Primary productivity in the SFE ranks towards the bottom of river-dominated estuaries (Boynton et al., 1982) and is thought to be regulated by turbidity and not nutrient supply (Cole and Cloern, 1984; Alpine and Cloern, 1988). However, recent studies suggest that in addition to light availability, increased nutrient loading (especially NH_4 loading) acts as an additional estuarine "filter" (Cloern, 2001) that modulates primary production and results in alterations to the food web (Glibert, 2010; Glibert et al., 2011). Spring and summer phytoplankton blooms (traditionally diatoms; Cloern and Dufford, 2005) were previously a regular feature in the Northern SFE but rarely occur now (Kimmerer, 2006;

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Wilkerson et al., 2006; Jassby, 2008). Suppression of SFE spring blooms was linked to elevated NH_4 concentrations (Wilkerson et al., 2006; Dugdale et al., 2007). When NH_4 concentrations were above 4 μmol N L^{-1}, high chlorophyll-a concentrations were not observed. Only when NH_4 was decreased below 4 μmol N L^{-1}, either through phytoplankton assimilation or through freshwater dilution, did phytoplankton access NO_3, the larger pool of dissolved inorganic nitrogen (DIN) and accumulate chlorophyll-a biomass (Dugdale et al., 2007). A bloom sequence consists of two phases and only occurs when irradiance conditions are favorable for phytoplankton growth. In the first phase, NH_4 is taken up by the phytoplankton resulting in reduction of ambient NH_4 concentrations to below about 4 μmol N L^{-1}. In the second phase, as NO_3 is taken up, chlorophyll-a biomass accumulates and blooms result (Dugdale et al., 2007).

The requirement for use of NO_3 to enable bloom formation in SFE, rather than NH_4 seems counter-intuitive to the classical paradigm that phytoplankton "prefer" NH_4 over NO_3 as a result of lower energetic costs to the cell associated with protein synthesis (McCarthy et al., 1977). While the energetic argument is correct and applies in most batch culture experiments in the laboratory, in the SFE NH_4 concentrations (e.g. winter mean in the Northern SFE = 6.8 μmol N L^{-1}; Wilkerson et al., 2006) are insufficient to fuel blooms. So for elevated chlorophyll-a concentrations, NO_3 (e.g. 27.5 μmol N L^{-1}; Wilkerson et al., 2006), the larger DIN pool, must be accessed. This can only be accomplished once NH_4 is below some threshold above which it is inhibitory to NO_3 uptake and assimilation. Raven et al. (1992) described how when both NO_3 and NH_4 are present (as in the SFE), phytoplankton will almost invariably use NH_4 with complete suppression of NO_3 uptake at NH_4 concentrations of as little as 1–2 μmol N L^{-1}. The suppression of phytoplankton NO_3 uptake by NH_4 has been documented in phytoplankton isolates (e.g. Cochlan and Harrison, 1991; Dortch, 1990; Lomas and Glibert, 1999; Maguer et al., 2007) and in natural communities (e.g. McCarthy et al., 1977; Collos et al., 1989; Cochlan and Bronk, 2003; L'Helguen et al., 2008).

The impact of NH_4 suppression of NO_3 uptake and the reduction of phytoplankton blooms and primary production is particularly important for the Northern SFE, where food limitation has been demonstrated for zooplankton (Mueller-Solger et al., 2002) and fish species (Bennett and Moyle, 1996) and may be in part responsible for an overall "pelagic organism decline" (Sommer et al., 2007). Glibert (2010) described how the decline in fish may be closely linked to historical changes in nutrient loadings, especially of NH_4 and P (Van Nieuwenhuse, 2007). Although the Sacramento River that feeds the Northern SFE has been considered a significant source of organic matter for the Northern SFE (Jassby et al., 2002; Sobczak et al., 2005), little is known or documented about productivity of the phytoplankton in the river and the impact of N loading on their physiology. The goals of this study were to: (1) understand the distribution and biological processing of different forms of DIN in the Sacramento River and (2) describe how discharge of wastewater NH_4 effluent influences phytoplankton biomass and primary productivity in the Sacramento River and downstream to the Northern SFE.

2. Materials and methods

2.1. River and estuary surveys

Two, 150-km surveys of the Sacramento River and Northern San Francisco Estuary were made on 26–27 March and 23–24 April 2009 using the R/V *Questuary*. During each survey 21 geographically fixed stations were sampled on the outgoing tide from upstream to downstream (Fig. 1 and Table 1). For analysis the transect was divided into six regions based on geographic location, ambient NH_4 and chlorophyll-a concentrations. The Upper River region included the four stations (I80, TOW, OAK and GRC) above the Sacramento Regional Wastewater Treatment Plant (SRWTP) and was characterized by low NH_4 concentrations (⩽1 μmol N L^{-1}). The SRWTP region included three stations (RM44, HOD and KEN), that were the closest geographically to the SRWTP and had elevated NH_4; RM44 is the station closest to the SRWTP discharge. The Central River region encompassed three stations (CRS, L37 and ISL) and also exhibited high NH_4 concentrations. The Lower River region included four stations (657, 655, 653 and 649) and was marked by declines in both NH_4 and chlorophyll-a concentrations. In the Northern estuary, Suisun Bay included six stations (US2, US3, US4, US5, US6 and US7) and San Pablo Bay was represented by a single station (US13). Stations south of Isleton (ISL) were identical to monthly water quality monitoring stations sampled by the US Geological Survey (USGS) (Jassby et al., 1997; http://sfbay.wr.usgs.gov/access/wqdata/index.html). River distances (km) were calculated from the SRWTP (i.e. at 0 km) with stations upstream of the SRWTP being negative. Sacramento River discharge was obtained from the California Department of Water Resources Dayflow algorithm (http://www.water.ca.gov/dayflow/). SRWTP daily effluent discharge was obtained from the California Central Valley Regional Water Quality Control Board.

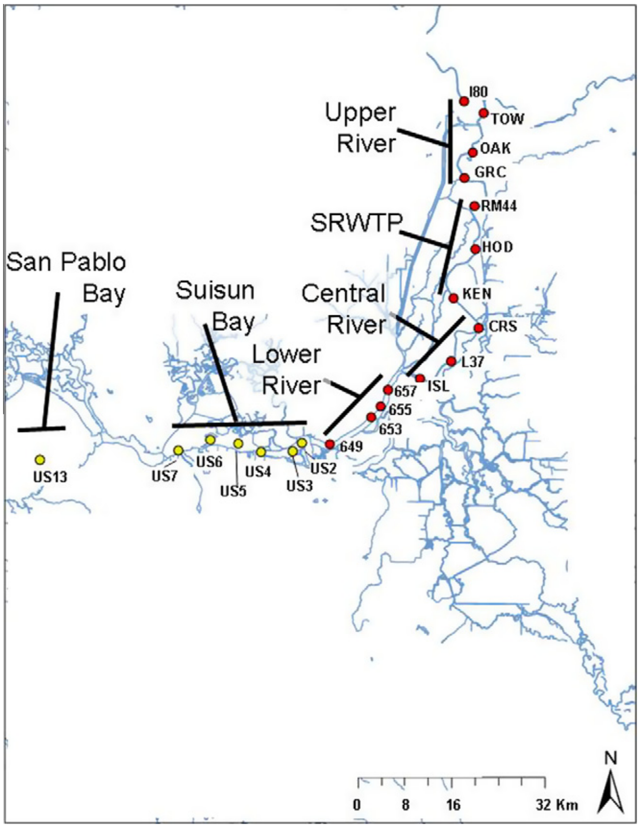

Fig. 1. Study region of the Sacramento River and San Francisco Estuary, CA showing sampling stations and river and Northern estuary transect regions.

At each station, a Seabird Electronics SB-32 rosette mounted with six 3-L Niskin bottles and fitted with a Seabird SBE-19 plus CTD was deployed to collect vertical profiles of temperature and salinity and collect surface water samples. In the freshwater regions the salinity was reported as electrical conductivity (μS cm^{-1}) while in the Northern SFE salinity was reported using the practical salinity scale (pss). Turbidity was measured with a D&A Instruments Optical Backscatter (Model OBS-3, S/N 937) sensor

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Table 1
Salinity, light attenuation coefficient and nutrient concentrations (mean ± SD) in Sacramento River and SF Estuary by river region (number of stations) for March and April 2009.

River Region	EC (μS cm^{-1})	k (m^{-1})	NO_3 (μmol L^{-1})	NO_2 (μmol L^{-1})	NH_4 (μmol L^{-1})	DIN (μmol L^{-1})	NH_4 as %DIN (%)	Urea (μmol L^{-1})	SRP (μmol L^{-1})	$Si(OH)_4$ (μmol L^{-1})
March 2009										
Upper River (4)	86 ± 8	2.5 ± 0.5	13.08 ± 0.59	0.12 ± 0.02	0.25 ± 0.09	13.81 ± 0.60	1.8	0.36 ± 0.07	1.37 ± 0.12	343 ± 19
SRWTP (3)	85 ± 5	3.2 ± 0.1	13.85 ± 1.46	0.15 ± 0.08	29.58 ± 10.24	43.87 ± 12.05	64.2	0.29 ± 0.38	2.94 ± 0.95	336 ± 4
Central River (3)	86 ± 2	3.5 ± 0.2	17.21 ± 2.16	0.35 ± 0.09	34.50 ± 8.29	52.43 ± 9.04	66.8	0.44 ± 0.38	3.14 ± 0.39	333 ± 11
Lower River (4)	117 ± 1	1.8 ± 0.3	29.07 ± 1.24	0.95 ± 0.10	13.76 ± 3.17	44.26 ± 3.93	31.2	0.44 ± 0.22	2.98 ± 0.16	350 ± 4
Suisun Bay (6)	0.9 ± 1.3[*]	1.3 ± 0.1	32.94 ± 0.5	1.19 ± 0.29	8.54 ± 1.20	43.23 ± 1.70	19.7	0.56 ± 0.40	2.96 ± 0.11	327 ± 14
San Pablo Bay (1)	23.1[*]	2.5	21.85	1.03	2.24	26.01	8.6	0.84	2.33	138
April 2009										
Upper River (4)	113 ± 11	1.0 ± 0.4	2.06 ± 0.54	0.14 ± 0.01	0.58 ± 0.23	2.78 ± 0.73	20.4	0.10 ± 0.20	0.44 ± 0.10	270 ± 34
SRWTP (3)	123 ± 4	1.4 ± 0.3	4.57 ± 0.95	0.21 ± 0.10	36.02 ± 13.47	40.80 ± 14.38	86.9	0.26 ± 0.25	1.70 ± 0.20	276 ± 13
Central River (3)	123 ± 4	1.1 ± 0.2	7.73 ± 2.08	0.42 ± 0.10	31.84 ± 13.35	39.99 ± 15.19	81.4	0.24 ± 0.14	1.81 ± 0.43	271 ± 10
Lower River (4)	144 ± 2	2.5 ± 0.7	18.29 ± 1.96	0.93 ± 0.07	14.57 ± 1.46	33.79 ± 0.58	44.6	0.08 ± 0.06	1.84 ± 0.15	276 ± 16
Suisun Bay (6)	2.6 ± 2.5[*]	3.0. ± 0.4	30.71 ± 2.35	1.35 ± 0.30	7.72 ± 0.96	39.78 ± 3.15	19.4	0.46 ± 0.46	2.32 ± 0.23	259 ± 19
San Pablo Bay (1)	24.6[*]	1.7	28.00	0.78	3.13	31.13	10.0	0.10	2.32	72

[*] Indicated salinity (dimensionless) reported on the practical salinity scale.

and reported as nephelometric turbidity units (ntu). The rosette was also equipped with a LiCor 4Π photosynthetically active radiation (PAR) sensor. Light attenuation, k (m^{-1}), was calculated by linear regression of log transformed PAR versus depth.

2.2. Detailed methods

20-ml dissolved inorganic carbon (DIC) samples were collected in glass scintillation vials, preserved according to Sharp et al. (2009) with 200 µL 5% w/v $HgCl_2$ and stored in the dark. These data were used for calculating ^{13}C uptake rates. DIC analysis was completed within 1 week using a Monterey Bay Research Institute – clone DIC analyzer with acid-sparging and a LiCor nondispersive infrared detector (Model 6252) (Friederich et al., 2002; Parker et al., 2006). Water samples for nutrient analysis were immediately filtered through Whatman GF/F filters using a 50-ml syringe and stored on dry ice in 20-ml HDPE scintillation vials or 50-ml centrifuge tubes. All nutrient analyses, except for NH_4 and urea–N, were performed on a Bran and Luebbe AutoAnalyzer II. NO_3, NO_2 and soluble reactive phosphorus (SRP) were analyzed using Whitledge et al. (1981) and $Si(OH)_4$ using Bran and Luebbe (1999) and MacDonald et al. (1986). Twenty-five milliliter samples for NH_4 determination were collected separately into 50-ml centrifuge tubes after filtration (Wilkerson et al., 2006). These samples were also immediately frozen for later analysis by the colorimetric method of Solorzano (1969) using a Hewlett Packard diode array spectrophotometer and 10-cm path length cell. Samples for urea were prepared in the same manner as NH_4 samples with analysis performed according to Revilla et al. (2005).

Two size fractions were collected for analysis of extracted chlorophyll-a concentration using 25-mm Whatman GF/F filters (nominally cells >0.7-µm, referred to here as the "whole community" fraction) and 25-mm diameter 5.0-µm Nuclepore pore-sized polycarbonate filters. Sample volumes were selected to minimize filtration times to <10 min using a low vacuum (<250 mm Hg) and varied between 50 and 200 ml. Filters were stored dry at 4 °C for up to one week. Prior to analysis, chlorophyll-a was extracted from the filters in 90% acetone for 24-h at 4 °C according to Arar and Collins (1992). Analysis was performed fluorometrically with a Turner Designs Model 10-AU using 10% hydrochloric acid to correct for and measure phaeophytin. The fluorometer was calibrated with commercially available chlorophyll-a (Turners Designs chlorophyll-a standard). Phaeophytin concentrations were calculated according to Holm-Hansen and Riemann (1978).

Phytoplankton carbon productivity and nitrogen (NO_3 and NH_4) uptake rates were estimated using dual-labeled $^{13}C/^{15}N$ tracer incubations (Legendre and Gosselin, 1996; Parker, 2005; Parker et al., submitted for publication). Two, 160-ml clear polycarbonate incubation bottles were filled with sample water at each station; to one incubation bottle $H^{13}CO_3$ and $^{15}NH_4Cl$ were added and to the other, $H^{13}CO_3$ and $K^{15}NO_3$ (all stable isotope stocks contained 99 at%, Cambridge Isotope Laboratories). Isotope additions were kept to ca 10% of ambient concentrations. Incubations were performed over 24-h on board in a flowing river water incubator covered with one layer of window screening to simulate 50% of ambient surface PAR. A 24-h period was selected so that incubations could be started throughout the day. Because DIN concentrations were generally high (>>2 µmol N L^{-1}) N-substrate limitation during incubations was unlikely at most stations as phytoplankton N uptake rates were generally <2 µmol N L^{-1} d^{-1}. We did not attempt to account for NH_4 regeneration and reported NH_4 uptake rates should be considered conservative. Incubations were terminated by gentle vacuum filtration onto pre-combusted (450 °C for 4-h) 25-mm diameter GF/F filters. Phytoplankton ^{13}C and ^{15}N enrichment, concentrations of particulate carbon (POC) and nitrogen (PON) were measured on a PDZ Europa 20/20 gas chromatograph – mass spectrometer. Carbon and nitrogen uptake rates (ρ, µmol L^{-1} d^{-1}) and biomass-specific uptake (normalized to either POC or PON, V, d^{-1}) were calculated according to Dugdale and Wilkerson (1986). Phytoplankton carbon uptake rates (ρC) are referred to as "primary production" as is the convention for carbon uptake studies.

During this study phytoplankton C and N uptake rates were measured only on surface samples incubated at 50% of surface PAR. To estimate a maximum depth-integrated NH_4 uptake rate for the SRWTP region, we multiplied the average surface NH_4 uptake rate by the euphotic zone depth. This procedure assumes a constant uptake throughout the euphotic zone and is likely an overestimate. The depth integrated water column NH_4 concentration at the SRWTP region was calculated using the mean surface concentration for the SRWTP region multiplied by the depth at the SRWTP station RM44 (8 m), assuming full vertical mixing.

To estimate microbial nitrification rates, a mass balance approach was used that calculated the increase in NO_3 concentrations measured between the SRWTP region (at KEN, Fig. 1) (NO_3 = 15.62 µmol N L^{-1}) and downstream in Suisun Bay at the location with the maximum NO_3 concentration (US5 = 34.00 µmol N L^{-1}). Using the mean March 2009 Sacramento River flow rate (850 m^3 s^{-1}, Fig. 2), the calculated river flow speed was ~13 km d^{-1}. Assuming no algal uptake of NH_4 and quasi-steady state conditions, the difference in NO_3 concentrations divided by the transit time between the locations was used to calculate a rate

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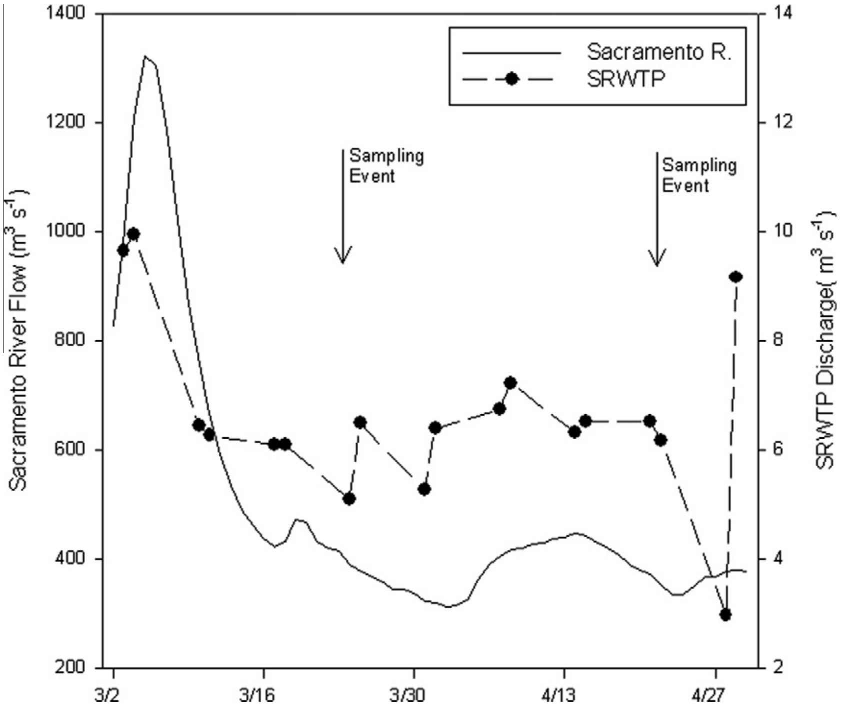

Fig. 2. Sacramento River flow (solid line) and Sacramento Regional Wastewater Treatment Plant (SRWTP) discharge (dashed line) during March and April 2009. Sampling event dates are indicated with arrows.

of NO_3 appearance (i.e. nitrification). An alternative approach from Yool et al. (2007) used an average specific nitrification factor to predict the µmol NO_3 L^{-1} produced per µmol NH_4 L^{-1} per day. This factor was applied to the maximal NH_4 concentration (40 µmol N L^{-1}) in the Sacramento River (at KEN).

3. Results

3.1. River and SRWTP discharge, temperature, salinity, turbidity and light attenuation

Based on the California Water Year Hydrologic Classification Index (http://cdec.water.ca.gov/cgi-progs/iodir/wsihist), 2009 was classified as a "dry" year. Sacramento River flow during March and April varied between 311 and 1322 m^3 s^{-1} with higher flow at the beginning of March (Fig. 2). SRWTP discharge represented roughly one percent of river flow (3–10 m^3 s^{-1}). Mean nitrogen load from the SRWTP was 15.5 ± 2.9 tons N d^{-1} during the study period (Central Valley Regional Water Quality Control Board, personal communication). Surface water temperature was similar between stations during the March survey, with an average (±SD) water temperature of 14.2 ± 0.3 °C (data not shown). During April, surface water temperatures were warmest in the Upper River, SRWTP and Central River regions (averaging 18.9 ± 0.4 °C; $n = 10$) and in the Lower River region (18.4 ± 0.6 °C, $n = 4$) and coldest in Suisun and San Pablo Bays (16.8 ± 1.0 °C, $n = 7$). In April, mean electrical conductivity (EC) was 113 ± 11 µS cm^{-1} in Upper River and 123 ± 4 µS cm^{-1} for both SRWTP, and Central River regions and then increased within the Lower River (144 µS cm^{-1}) and into Suisun Bay (2.6 psu) (Table 1). The downstream decrease in water temperatures with increased salinity during April was due to mixing with ocean water. During March, EC showed a similar pattern although values were generally lower. Vertical profiles of temperature, salinity and turbidity suggest a well mixed water column in the Upper River (I-80), SRWTP (RM44), Central River (L37) and Lower River (US657) regions (Fig. 3). Stations within Suisun Bay (US4) and San Pablo Bay (US13) showed some vertical structure, with slightly colder temperatures and higher salinity with depth. Turbidity showed increases at depth at these two stations suggesting higher suspended sediment loads.

Light attenuation coefficients for the different regions varied between 1.3–3.5 m^{-1} for March and 1.0–3.0 m^{-1} for April (Table 1). Using all data from March and April transects, k and turbidity were strongly correlated ($k = 12.2 * \text{ntu} + 0.62$; $r^2 = 0.91$, $p < 0.0001$, $n = 42$; data not shown). Similar analysis of k versus chlorophyll-a did not show a significant relationship ($r^2 = 0.02$, $p = 0.65$, $n = 42$, data not shown), indicating that phytoplankton biomass and light attenuation were not related. Because sampling was generally restricted to the main navigational channel of the estuary and river, the ratio of water column depth to euphotic zone depth (i.e. to 1% of surface PAR) was relatively high indicating generally poor average light conditions for phytoplankton throughout the well mixed water column. This ratio averaged 2.5 for the Upper River, SRWTP and Central River regions, 5.9 for the Lower River region, 10.8 for Suisun Bay and 4.8 for San Pablo Bay. At two locations (I80 and ISL) during April the water column depth (<5 m) was less than the euphotic zone depth such that sunlight likely penetrated to the river bottom, providing a more favorable light environment for phytoplankton.

3.2. Nutrient concentrations

The effect of the SRWTP effluent on NH_4 concentrations was apparent during March and April, first as a large step increase in NH_4 between the Upper River and the SRWTP region at station RM44 followed by peak values in the Central River region (Fig. 4A, B). NH_4 concentrations declined going downstream to the Lower River region and remained relatively low through Suisun Bay. NO_3 concentrations remained relatively constant from the Upper River, SRWTP and Central River regions, and then increased rapidly to the Lower River. Dissolved inorganic nitrogen (DIN) concentrations were lower in all transect regions during April

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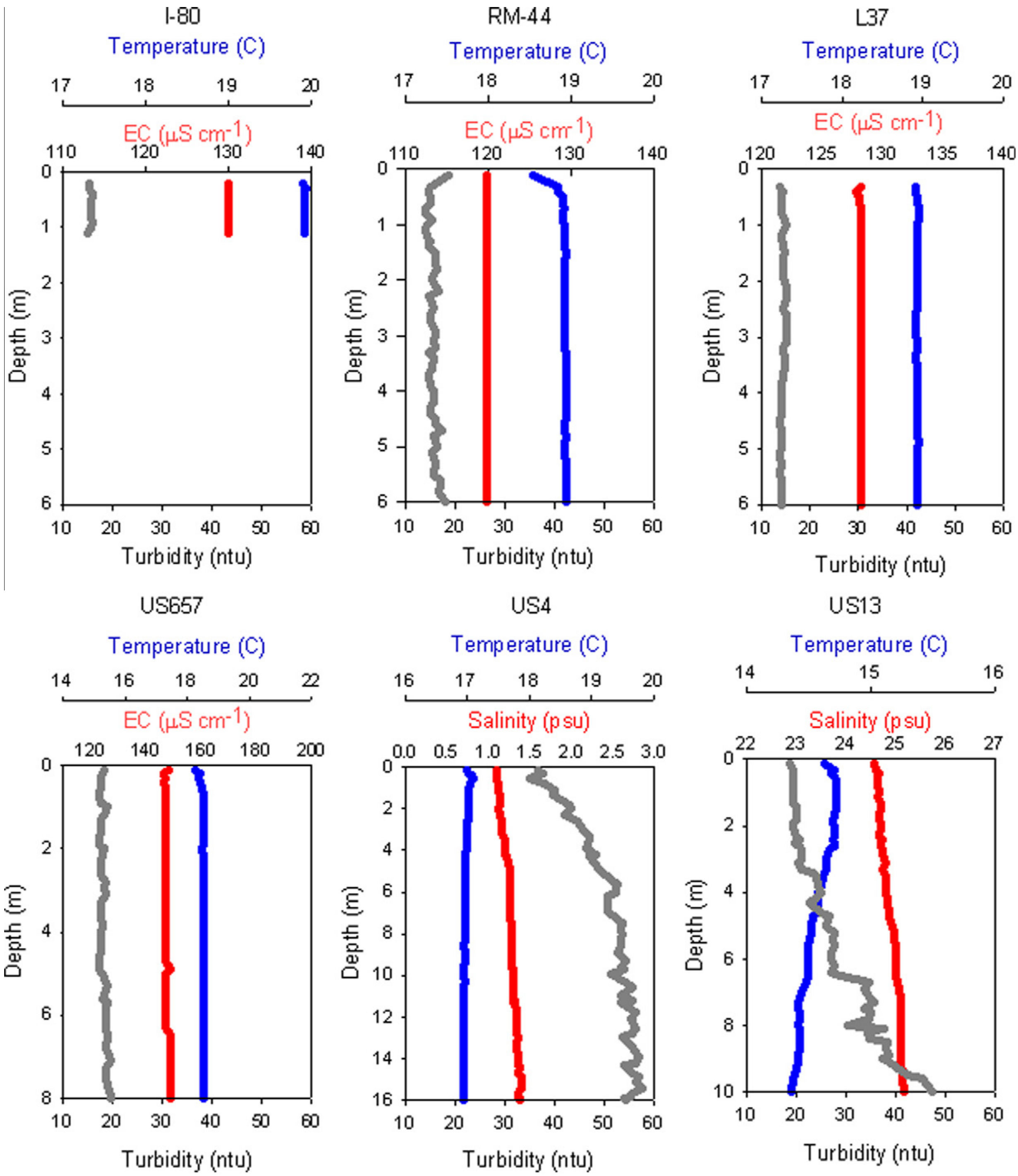

Fig. 3. Vertical profiles of temperature (blue), electrical conductivity or salinity (red) and optical backscatter (gray) in April 2009 from stations representing six regions in the Sacramento River and the Northern San Francisco Estuary.

compared to March except for San Pablo Bay. This difference between months was most pronounced in the Upper River Region where the DIN concentration (mostly NO_3) in March was 4-fold greater than April (Table 1 and Fig. 4A, B). In the Upper River during both months, NH_4 was low (<1 μmol N L^{-1}), but since NO_3 varied between months in the Upper River, NH_4 contributed between 1.8% in March to 20.4% in April to the DIN pool (Table 1). In the SRWTP and Central River regions the percent NH_4 increased from 64.2% to 86.9%. The contribution of NH_4 to total DIN decreased to 31.2% to 44.6% in the Lower River region, to <20% in Suisun Bay and to ⩽10% in San Pablo Bay.

NO_2 concentrations were generally low (<2 μmol N L^{-1}) relative to NO_3 and NH_4 along both surveys (Table 1 and Fig. 4A, B). However, a consistent increase in NO_2 occurred within the Lower River and Suisun Bay (Table 1 and Fig. 4A, B). The highest region-mean NO_2 concentrations (1.19 and 1.35 μmol N L^{-1}, for March and April, respectively) were observed within the Suisun Bay region (Table 1). Urea concentrations were always <1.0 μmol N L^{-1} (Table 1). A large increase in SRP concentration was observed during both surveys at RM44, suggesting that the SRWTP was a significant source of SRP for the river (Table 1 and Fig. 4A, B). Downstream SRP concentrations followed the downstream changes in DIN during both

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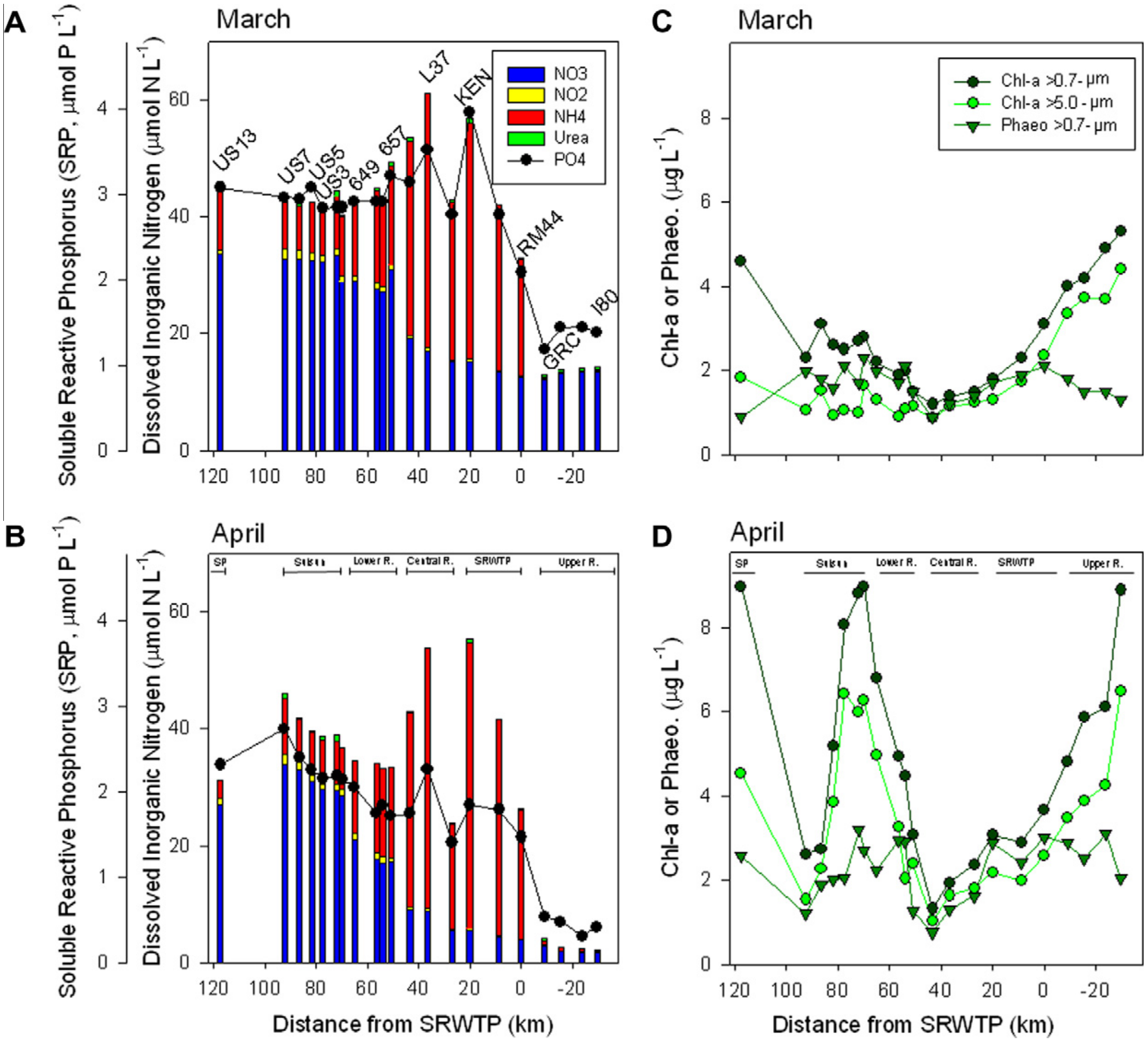

Fig. 4. Inorganic nutrient concentrations measured in the Sacramento River and Northern SFE in (A) March and (B) April 2009 (NO_3; blue, NO_2; yellow, NH_4; red, urea–N; green, SRP; black). Concentrations of chlorophyll-a in cells >0.7-μm diameter (closed circle) and >5.0-μm (open circles) and phaeophytin >0.7-μm (inverted triangles) during (C) March and (D) April 2009.

months. Silicate concentrations declined with distance along the transect, and were generally inversely related to salinity.

3.3. Chlorophyll-a concentrations

The downstream distribution of chlorophyll-a followed similar patterns for both surveys (Fig. 4C and D) but concentrations were higher during April compared to March (Table 2 and Fig. 4C, D). Chlorophyll-a for the whole community (>0.7-μm fraction) decreased downstream from the Upper River region (4.6 ± 0.6 and 6.4 ± 1.7 μg L^{-1} in March and April, respectively) through the Central River region where the lowest chlorophyll-a concentrations were observed (1.4 ± 0.2 and 1.9 ± 0.5 μg L^{-1}; Table 2 and Fig. 4C, D). Chlorophyll-a then increased in the seaward direction from the Lower River region to Suisun Bay and San Pablo Bay (maximum values of 4.6 and 9.0 μg L^{-1} at San Pablo Bay, Table 2 and Fig. 4C, D). Chlorophyll-a in the larger cells (i.e. >5-μm in diameter) showed a similar pattern to whole community chlorophyll-a along both surveys (Fig. 4C and D). At most locations the larger cell-sized fraction contributed more than 60% to the total chlorophyll-a (Table 2). However, in March, in the Lower River region and seaward, the percentage of chlorophyll-a in the larger cells was lower (Table 2). Phaeophytin concentrations paralleled that of chlorophyll-a throughout most of the surveys except in the Upper River region where they decreased as chlorophyll-a increased upstream (Fig. 4C and D).

3.4. Primary production and nutrient uptake

Consistent with chlorophyll-a concentrations, rates of primary production (ρC) were lower during the March survey compared to April likely in response to the seasonal increase in solar irradiance (Table 2 and Fig. 5A, B). The primary production pattern followed the changes in the nitrogen source being accessed and taken up (Fig. 5A and B). The highest river primary production rates were observed in the Upper River region where NO_3 was being taken up (Fig. 5A and B) and.NH_4 concentrations were low (Fig. 5C and D). Accompanying elevated NH_4 concentrations in the SRWTP region, phytoplankton NO_3 uptake ceased and phytoplankton NH_4 uptake increased (Fig. 5A and B). With the elevated NH_4 concentrations downstream of the SRWTP (Fig. 5C and D), phytoplankton NO_3 uptake was negligible (Fig. 5A and B). Primary production and phytoplankton NH_4 uptake declined downstream to minima within the Lower River region in March and the Central River region during April. Primary production increased in Suisun Bay (Table 2) as NH_4 concentrations declined (Fig. 5C and D) and both

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Table 2
Chlorophyll concentrations and carbon uptake (mean ± SD) in Sacramento River and SF Estuary by river region (number of stations) for March and April 2009.

River Region	Chl-a in cells >0.7-µm (µg L^{-1})	Chl-a in cells >5.0-µm (µg L^{-1})	% Chl-a in cells >5.0-µm (µg L^{-1})	ρC (µmol L^{-1} d^{-1})	Assimilation.Number (µmol $L^{-1}d^{-1}$(µg chl-a)$^{-1}$)	ρC as % of Upper River (%)	VC (d^{-1})
March 2009							
Upper River (4)	4.6 ± 0.6	3.8 ± 0.4	83	14.13 ± 1.34	3.07		0.15 ± 0.03
SRWTP (3)	2.4 ± 0.6	1.8 ± 0.5	75	8.47 ± 1.77	3.53	60	0.08 ± 0.02
Central River (3)	1.4 ± 0.2	1.1 ± 0.2	79	5.38 ± 0.59	3.87	38	0.06 ± 0.00
Lower River (4)	1.9 ± 0.3	1.1 ± 0.1	58	4.47 ± 1.30	2.35	32	0.03 ± 0.06
Suisun Bay (6)	2.7 ± 0.3	1.2 ± 0.3	44	9.39 ± 1.26	3.47	64	0.05 ± 0.01
San Pablo Bay (1)	4.6	1.8	39	24.11	5.24	171	0.29
April 2009							
Upper River (4)	6.4 ± 1.7	4.5 ± 1.3	70	36.32 ± 8.50	5.68		0.31 ± 0.07
SRWTP (3)	3.2 ± 0.4	2.3 ± 0.3	72	18.02 ± 4.62	5.63	50	0.13 ± 0.04
Central River (3)	1.9 ± 0.5	3.4 ± 0.4	69	11.01 ± 1.52	5.79	30	0.11 ± 0.00
Lower River (4)	4.5 ± 1.5	2.9 ± 1.2	64	13.66 ± 3.58	3.03	38	0.08 ± 0.02
Suisun Bay (6)	6.1 ± 3.0	4.4 ± 2.2	72	21.59 ± 9.19	3.50	59	0.09 ± 0.03
San Pablo Bay (1)	9.0	4.5	50	36.07	4.00	99	0.30

phytoplankton NO_3 and NH_4 uptake also increased (Table 3 and Fig. 5A, B). Primary production was highest in San Pablo Bay (24.11 and 36.07 µmol C L^{-1} d^{-1} for March and April, respectively) relative to other locations along the survey (Table 2 and Fig. 5A, B). Primary productivity showed a U-shaped pattern with peaks at each end of the transect. Nitrogen uptake showed the same downstream U-shaped pattern with peak NO_3 uptake rates in the Upper River and San Pablo Bay (Table 3 and Fig. 5A, B).

Additional insight into the underlying physiological mechanisms of the phytoplankton can be obtained from the biomass-specific C and N uptake rates (VC or VN) from the Upper River region to San Pablo Bay (Fig. 5C and D). Unlike ρC and ρN, VC and VN do not reflect any changes in biomass as seen with chlorophyll-a along the surveys but indicate physiological changes. Still, similar U-shaped patterns, consistent with that observed for chlorophyll-a concentrations and phytoplankton C and N uptake rates (ρC and ρN), were observed for VC and VN. This U-shape was an inverse pattern to that of NH_4 concentration. The transition from a NO_3 uptake-based phytoplankton population to one based on NH_4 uptake is seen in the progression from Upper River to the SRWTP region. In the Upper River region, high VNO_3 of 0.3 d^{-1} implies a doubling time of the phytoplankton population of about 3 days, based on NO_3 uptake. At the SRWTP region, VNO_3 decreased dramatically to near-detection limits and VNH_4 increased, accompanying increased NH_4 concentration. VNH_4 then declined downstream as NH_4 concentrations increased further. From the Lower River region to Suisun Bay, VNO_3 remained low and unchanged, and VNH_4 was either unchanged (March) or increased (April). Peak specific carbon uptake (VC) coincided with peak VNO_3 in the Upper River region and in San Pablo Bay where NH_4 concentrations were lowest. Within the Sacramento River downstream of the Upper River region, VC rates declined, reaching near zero in the Lower River during March, paralleling the decrease in VNH_4.

The elevated NH_4 concentrations introduced in the SRWTP region were related negatively to both phytoplankton NO_3 and NH_4 uptake (Fig. 6A and B). Biomass-specific NO_3 uptake decreased exponentially with increasing NH_4 concentrations, starting at <2 µmol NH_4 L^{-1} (Fig. 6A). Biomass-specific NH_4 uptake versus NH_4 concentration showed a complex pattern with indications of inhibition of VNH_4 at both low and high NH_4 concentrations (Fig. 6B). Within the SRWTP and Central River regions where effluent is first introduced to the Sacramento River, linear regression analysis shows VNH_4 was negatively correlated with NH_4 concentration for both transects, with nearly identical regression slopes (−0.0031 and −0.0039) and high r^2 values, indicating that effluent NH_4 decreased NH_4 uptake (Fig. 6B). At other locations within the river, there was no correlation between VNH_4 and NH_4 concentration.

Estimates of depth-integrated phytoplankton NH_4 uptake (4.65 mmol NH_4 m^{-2} d^{-1}) and water column NH_4 concentration (288.16 mmol N m^{-2}) in the SRWTP region were calculated for April 2009 using the mean surface ρNH_4 uptake of 1.41 µmol N L^{-1} d^{-1}; Table 3) multiplied by a euphotic zone depth of 3.3 m and the mean surface NH_4 concentration of 36. 02 µmol N L^{-1} multiplied by 8 m (the depth at RM44). The proportion of the water column NH_4 taken up by the phytoplankton was then estimated to be 4.65 mmol N m^{-2} d^{-1}/288.16 mmol N m^{-2} = 0.016 d^{-1} or 1.6% of the water column NH_4 each day. A river nitrification rate, estimated using the mass balance approach for increasing NO_3 downstream, was 4.0 µmol N L^{-1} d^{-1}. Using the average specific nitrification factor, nitrification was estimated to be 6.4 µmol N L^{-1} d^{-1}. Assuming a fully mixed water column of 8 m depth translates to a depth integrated rate of 32.0–51.2 mmol N m^{-2} d^{-1}.

4. Discussion

4.1. Depressed primary production in the Sacramento River

The Sacramento River has been thought to be a source of organic carbon to the Northern SFE (Jassby et al., 2002; Sobczak et al., 2005; Lehman et al., 2008). However the data reported here, similar to the limited primary production estimates for the main channel provided by Lehman et al. (2008), indicate that primary production and phytoplankton biomass in the Sacramento River in spring are actually lower than rates and stocks found in the Northern SFE (including in the well-described low productivity region of Suisun Bay, e.g. Kimmerer, 2005; Wilkerson et al., 2006).

Primary production in the Upper River region was relatively high (equivalent to <70% to ca. 100% of the rates measured in San Pablo Bay) but was strongly depressed in the middle section of the river. At the SRWTP region, primary production decreased by more than 50% compared to the Upper River region. Primary production in the Central River and Lower River regions were the most strongly depressed but began to increase again through Suisun Bay. This generalized U-shaped downstream spatial pattern of primary production was consistent between the two surveys. Clearly, the river is not a significant source of phytoplankton derived organic carbon to Suisun Bay as both primary productivity and chlorophyll-a concentrations are higher in Suisun Bay than in the inflowing river water. These results are in stark contrast to historic phytoplankton surveys of the Sacramento River made during the 1960's when phytoplankton stocks gradually increased moving downstream with highest abundances found at Isleton (ISL). At that time the phytoplankton community in the river was dominated by diatoms (Greenberg, 1964). While phytoplankton

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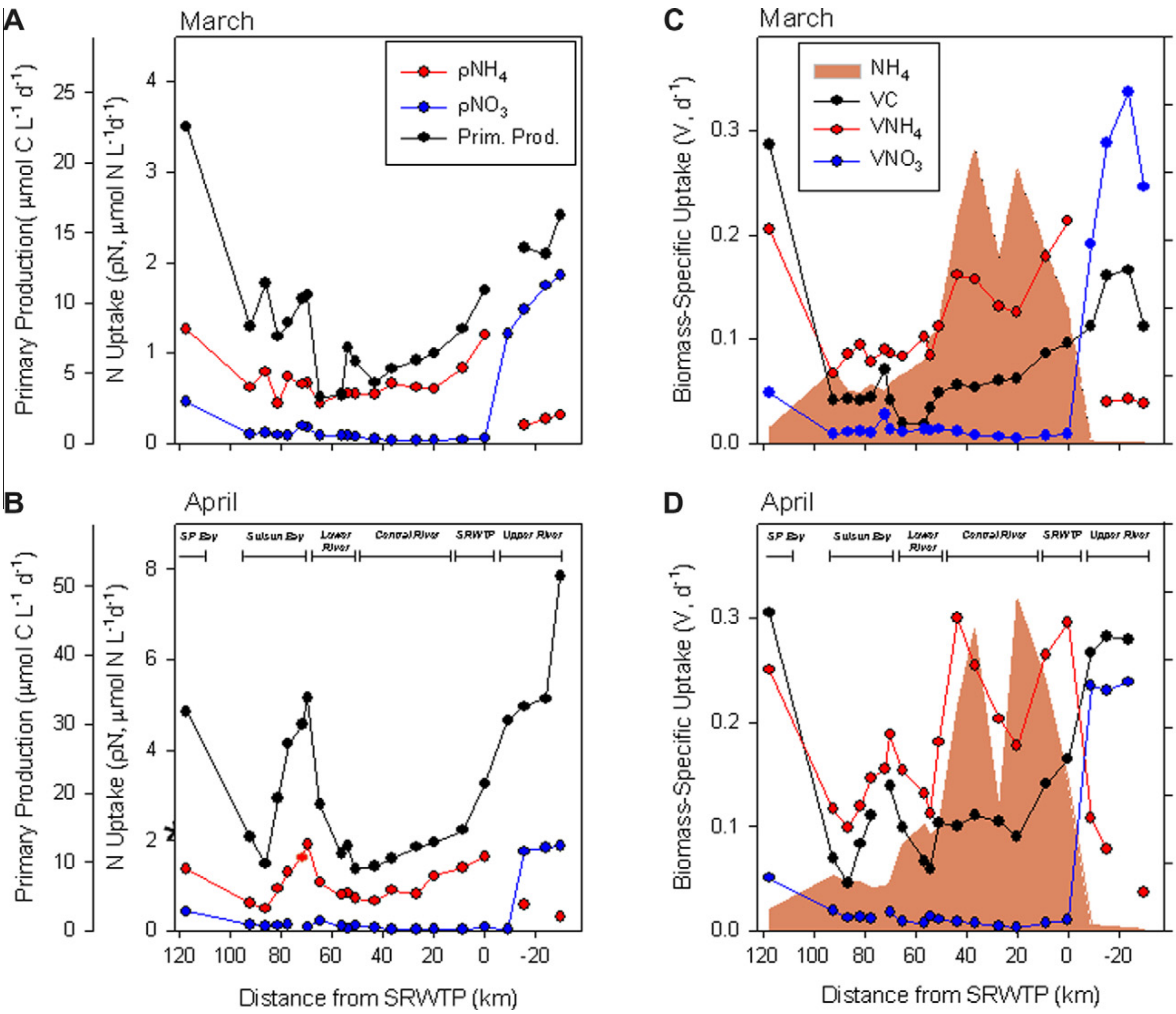

Fig. 5. Primary production and phytoplankton nitrogen uptake in the Sacramento River and Northern SFE during (A) March and (B) April 2009. Biomass-specific carbon uptake and phytoplankton nitrogen uptake and NH_4 concentrations (shaded area) during (C) March and (D) April 2009. *Y*-axes for phytoplankton C and N uptake are scaled at 6.6 C:1 N (i.e. the Redfield ratio).

Table 3
Ammonium and nitrate uptake (mean ± SD) in Sacramento River and SF Estuary by river region (number of stations) for March and April 2009.

River Region	ρNH_4	ρNO_3	% NO_3 uptake %	VNH_4	VNO_3
	$\mu mol\ N\ L^{-1}\ d^{-1}$			d^{-1}	
March 2009					
Upper River (4)	0.26 ± 0.06	1.57 ± 0.29	86	0.04 ± 0.00	0.27 ± 0.06
SRWTP (3)	0.88 ± 0.30	0.04 ± 0.01	4	0.18 ± 0.05	0.01 ± 0.00
Central River (3)	0.61 ± 0.06	0.04 ± 0.01	6	0.15 ± 0.02	0.01 ± 0.00
Lower River (4)	0.50 ± 0.08	0.08 ± 0.04	14	0.10 ± 0.02	0.01 ± 0.00
Suisun Bay (6)	0.65 ± 0.13	0.12 ± 0.05	16	0.11 ± 0.05	0.01 ± 0.01
San Pablo Bay (1)	1.26	0.46	27	0.21	0.05
April 2009					
Upper River (4)	0.44 ± 0.19	1.82 ± 0.05	81	0.06 ± 0.03	0.23 ± 0.00
SRWTP (3)	1.41 ± 0.21	0.06 ± 0.03	4	0.25 ± 0.06	0.01 ± 0.00
Central River (3)	0.80 ± 0.12	0.03 ± 0.01	4	0.25 ± 0.05	0.01 ± 0.00
Lower River (4)	0.86 ± 0.15	0.08 ± 0.03	9	0.14 ± 0.03	0.01 ± 0.00
Suisun Bay (6)	1.15 ± 0.56	0.14 ± 0.05	11	0.14 ± 0.03	0.02 ± 0.00
San Pablo Bay (1)	1.36	0.43	24	0.25	0.05

species were not enumerated during this study, the same stations were occupied during spring 2010 and showed a mixed phytoplankton community in the upper river (with diatoms comprising ~40% of the cells) to a community dominated (~80%) by small flagellates and green algae below the SRWTP region (Kress, personal communication) and with diatoms in Suisun and San Pablo Bays (Dugdale et al., submitted for publication).

Because light attenuation is largely explained by turbidity, the potential role that turbidity plays in the present results can be explored using euphotic zone depth. The ratio of river depth to

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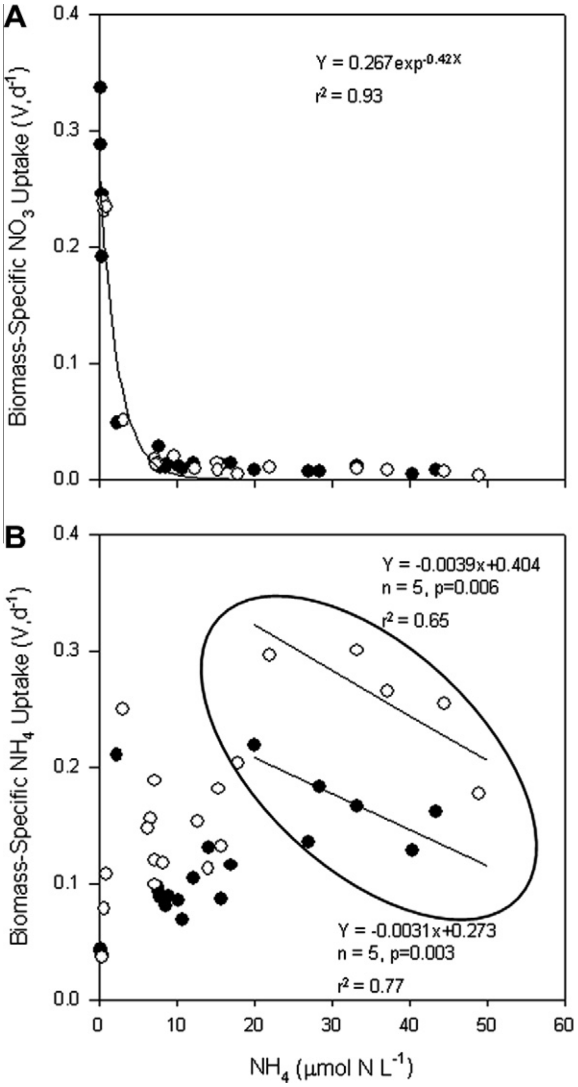

Fig. 6. Effect of NH_4 concentration on phytoplankton N uptake processes in the Sacramento River and Northern Sacramento River. (A) Biomass-specific NO_3 uptake rate (VNO_3) and (B) biomass-specific NH_4 uptake rate (VNH_4) versus NH_4 concentrations measured during March (closed circles) and April (open circles) 2009. Linear regression shown in panel B is based on the five stations occupied in the SRWTP and Central River regions (RM44, HOD, KEN, L37, ISL).

euphotic zone depth (i.e. critical depth, Sverdrup, 1953) does not explain chlorophyll-a trends in the Sacramento River. For example, within the Central River region, the photic zone extended to >70–100% of the river depth (i.e. phytoplankton-received solar energy throughout the water column), yet neither chlorophyll-a or primary production increased there. In contrast, in the eastern end of Suisun Bay water column depth increased significantly (up to 20-m), increasing the ratio of water depth to euphotic zone. This should result in decreased productivity and chlorophyll-a, yet chlorophyll-a and primary production were higher at these locations compared to shallower regions.

The declining productivity and NH_4 uptake conditions in the Sacramento River and Suisun Bay is comparable to observations in other river, estuarine and coastal ecosystems impacted by wastewater effluent (Waiser et al., 2011; Yoshiyama and Sharp, 2006; MacIsaac et al., 1979). In the Delaware Estuary which exhibits a similar range in both primary productivity and NH_4 concentrations (Yoshiyama and Sharp, 2006) a decline in the assimilation number (carbon uptake per unit chlorophyll-a) was associated with NH_4 concentrations >10 $\mu mol\ N\ L^{-1}$ (Yoshiyama and Sharp, 2006). In the Sacramento River, assimilation number declined by 43–47% from the Upper River to the Lower River and in March mean primary production (Table 2) decreased by a factor of ~3 from the highest values at the Upper River region to the lowest value in the Lower River region.

4.2. Effect of NH_4 on river primary production and nutrient uptake

The U-shaped spatial pattern of chlorophyll-a, primary production and phytoplankton N uptake are the mirror of NH_4 concentrations, and appear to be linked to the form of DIN being used by phytoplankton for growth, and by inhibition of NO_3 uptake by NH_4. The overall pattern that emerges is (1) high productivity at the upper end of the transect, associated with NO_3 uptake, (2) a mid-river region (Central River) in which primary production follows NH_4 uptake and NO_3 uptake is shut-down and NH_4 uptake is inhibited (by the high NH_4 concentrations), (3) elevated productivity in Suisun Bay and San Pablo Bay where both NO_3 and NH_4 fuel productivity.

This pattern and its relation to ambient NH_4 are better visualized in plots (Fig. 7A–F) of mean uptake rates for the different transect regions (Tables 2 and 3) versus mean NH_4 concentration (Table 1). The patterns for ρNO_3 versus NH_4 for March and April transects (Fig. 7A) are similar with an immediate decline in uptake from the relatively high levels in the Upper River to very low levels at the SRWTP and the Central River as NH_4 concentrations increase to 30–35 $\mu mol\ N\ L^{-1}$. ρNO_3 remains low in Lower River as NH_4 concentrations decrease and then increases in Suisun Bay and San Pablo Bay with further decreases in NH_4. When NO_3 uptake is normalized to the mean Upper River value for March (Fig. 7B), the patterns are virtually identical for the two transects sampled one month apart. The progression of ρNH_4 (Fig. 7C) shows an opposite pattern to ρNO_3 uptake, initially low in the Upper River at low NH_4 concentration, increasing to a peak at SRWTP with effluent NH_4 input, decreasing to Central River and Lower River, and finally increasing at Suisun Bay and San Pablo Bay at the lowest NH_4 concentration. The pattern is similar for March and April, especially apparent when normalized to mean Upper River ρNH_4 values for March (Fig. 7D). Carbon uptake, ρC (based upon the combined uptake of NH_4 and NO_3) when plotted against NH_4 concentration (Fig. 7E), decreases 50–60% from the Upper River to the SRWTP region with high effluent NH_4 (Table 2). A further decrease (to 30–38% of Upper River values) occurs in the Central River with increased NH_4. Carbon uptake remains low in the Lower River as NH_4 declines. Finally, ρC increases in Suisun Bay to 59–64% of the Upper River carbon uptake as NH_4 declines further (Fig. 7E) and NO_3 uptake begins to increase (Fig. 7A). The normalized plot for ρC versus NH_4 shows that the patterns for March and April are almost identical (Fig. 7F). The result is little assimilatory capacity of the river DIN by the phytoplankton and flux of NH_4 and NO_3 and little organic carbon to the Northern estuary.

Diminished estuarine productivity and the lack of spring phytoplankton blooms in Suisun Bay was attributed to the inability of the phytoplankton to access the largest inorganic N pool that was NO_3, due to NH_4 inhibition (Wilkerson et al., 2006; Dugdale et al., 2007). This apparently occurred also in the Sacramento River (Fig. 5) where there was high primary production at low NH_4 concentrations and phytoplankton N demand was satisfied by NO_3. Although phytoplankton use NH_4 before NO_3, sometimes referred to as a "preference" for NH_4 (McCarthy et al., 1977), some diatoms require NO_3 over NH_4 under some conditions (Glibert et al., 2004, 2006). Reduced primary production was associated with high NH_4 concentrations and the inhibition of phytoplankton NO_3 uptake. The decrease in phytoplankton NO_3 uptake with increasing river NH_4 concentration is consistent with many previous studies

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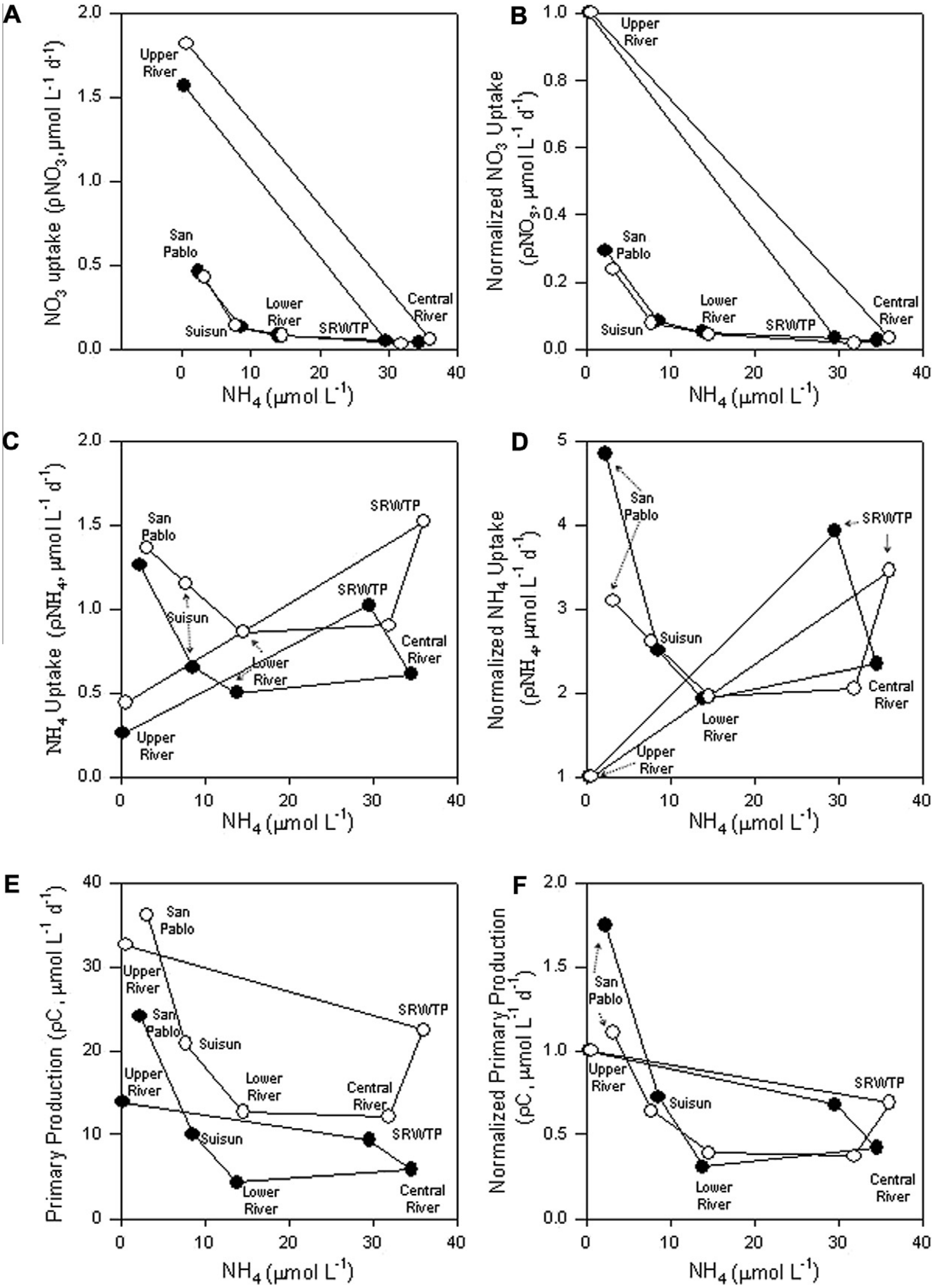

Fig. 7. River and estuary region means of C, NO_3 and NH_4 uptake versus NH_4 concentrations in the Sacramento River and the Northern SFE. (A, C, E) nitrate uptake (ρNO_3), ammonium uptake (ρNH_4), and carbon uptake (ρC). (B, D, F) The same data with uptake rates normalized to Upper River region mean uptake (ρ) rates.

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(Dortch, 1990), including those made in the SFE (Dugdale et al., 2007), Hong Kong waters (e.g. Xu et al., 2011) and coastal waters (Dugdale et al., 2006). An exponential function is often used to describe the inhibition of NO_3 uptake by NH_4 (e.g. Cochlan and Harrison, 1991) and this approach fit the data well here suggesting that NH_4 is the major factor in the reduced NO_3 uptake (Fig. 6A).

Another contribution to the depression in primary production and the decrease in chlorophyll-a in the river may be NH_4 inhibition of phytoplankton NH_4 uptake (Syrett, 1981). Suppression of VNH_4 immediately downstream of the SRWTP discharge was related to increased NH_4 concentrations (Fig. 6B). Two situations apparently exist within the Sacramento River. In the SRWTP and Central River regions where wastewater NH_4 discharge is most pronounced, phytoplankton NH_4 uptake is negatively correlated with NH_4 concentration. At other locations this does not occur. We are aware of at least one study that showed inhibition of both phytoplankton NH_4 uptake and primary production with additions of sewage effluent containing primarily NH_4 (MacIsaac et al., 1979). It is unclear in the present study whether NH_4 or some other component of the sewage effluent (of which NH_4 concentrations act as a "tracer") is responsible for the relationship observed here between VNH_4 and NH_4 concentrations although experimental additions of SRWTP effluent into Sacramento River water collected upstream of SRWTP influence showed the same result (Parker et al., 2009). The combination of these effects and resultant depression in primary production result in unused nutrients passing downstream of the Sacramento River and into Suisun Bay.

4.3. *Effect of phytoplankton assimilation and nitrification on Sacramento River NH_4 concentrations*

The extent to which phytoplankton NH_4 assimilation contributes to the decline in NH_4 concentrations downstream from the SRWTP can be estimated, as can microbial transformations such as nitrification (ammonia oxidation). With a river transport time of about 4 days from the SRWTP to the entrance of Suisun Bay, phytoplankton NH_4 uptake would account for only 6% of the water column NH_4 concentrations found in the SRWTP region. Based on this analysis, using a maximal estimate of the vertically integrated NH_4 uptake, phytoplankton have only a negligible influence on river NH_4 concentration as it flows downstream.

An additional, potentially important sink for anthropogenic NH_4 entering the Sacramento River is nitrification. This is the sequential oxidization of NH_4 to NO_2 and NO_3 to support chemosynthesis and is carried out in estuaries by NH_4-oxidizing bacteria and some archaea (e.g. AOA, Francis et al., 2005; Caffrey et al., 2007). Hager and Schemel (1992) showed that increases in NO_3 were correlated with decreases in NH_4 in the Sacramento River and inferred that nitrification might be a cause. A similar pattern was observed during this study, with elevated NH_4 at the SRWTP region that decreased, while NO_3 increased toward Suisun Bay. In the region where there was the greatest decrease in NH_4 and increase in NO_3, the intermediate inorganic N form, NO_2 was observed also suggesting that nitrification was occurring (Fig. 4A and B). Dark incubations using water collected at RM44 showed little conversion of NH_4 to NO_3 on time scales of seven days but appreciable NO_3 increase after 14 days (data not shown); the time lag for conversion of NH_4 to NO_3 may reflect low initial populations of AOA in the river upstream of the SRWTP region (Pauer and Auer, 2000). Using variation in the natural abundance of ^{15}N in NO_3 and NH_4, Kendall observed declining $\delta^{15}N–NO_3$ and increasing $\delta^{15}N–NH_4$; in the river below the SRWTP; evidence of nitrification with indications of strong nitrification in the vicinity of US657 (Kendall, personal communication).

Our two estimates of Sacramento River nitrification rates give a range (4.0–6.4 $\mu mol\ N\ L^{-1}\ d^{-1}$) comparable to other eutrophic systems that translates to a depth integrated rate of 32–51.2 $mmol\ N\ m^{-2}\ d^{-1}$ assuming a fully mixed water column of 8 m depth. Lipschultz et al. (1986) estimated July–September nitrification in the highly eutrophic region of the Delaware River of 0.08–0.47 $\mu mol\ N\ L^{-1}\ h^{-1}$ (or 1.9–11 $\mu mol\ N\ L^{-1}\ d^{-1}$). Feliatra and Bianchi (1993) measured nitrification rates of 0.23–2.15 $\mu mol\ N\ L^{-1}\ d^{-1}$ in the Rhone River where NH_4 concentrations varied between 1 and 10 $\mu mol\ N\ L^{-1}$. While the present estimates of nitrification for the Sacramento River are crude, the measured water column NH_4 uptake rate by phytoplankton is 9.1–14.5% of the inferred nitrification rate, indicating that nitrification may be the more significant biological process affecting the fate of NH_4 in the Sacramento River. Direct measurements of water column nitrification for the Sacramento River are needed.

Both nitrification and phytoplankton N uptake processes influence the concentrations of NH_4 downstream in the river. However, the sum of the two processes, at most 8 $\mu mol\ N\ L^{-1}\ d^{-1}$, are insufficient to prevent the export of substantial effluent-derived NH_4 to Suisun Bay and other seaward embayments of the Northern SFE. The NH_4 resulting from SRWTP effluent combined with phytoplankton nutrient assimilation and potential nitrification results in a mirror pattern of NH_4 concentration to the downstream U-shaped pattern of phytoplankton uptake and productivity. The delivery of NH_4 to the Northern SFE potentially impacts the pelagic food web and the success of pelagic fishes in this ecosystem.

5. Conclusions

Wastewater discharge from the Sacramento Regional Wastewater Treatment Plant fundamentally changes the microbial processes and biogeochemistry of the river as well as the receiving waters of the San Francisco Estuary and Delta. This study shows the importance of the effluent NH_4 contribution to the DIN pool used by river and estuarine phytoplankton. Three observations have been identified that show how wastewater discharge has changed the chemistry and biology of the river: (1) The secondary-level treatment in the wastewater results in substantial NH_4 concentrations in the Sacramento River downstream of the sewage discharge point. (2) Elevated NH_4 concentrations prevent access by the phytoplankton to high concentrations of NO_3 by inhibiting uptake, suppressing NH_4 uptake and depressing primary production downstream to Suisun Bay. (3) Phytoplankton NH_4 uptake rates and nitrification rates within the Sacramento River are insufficient to appreciably reduce NH_4 concentrations within the river, resulting in significant NH_4 loading to the Northern SFE, suppressing phytoplankton blooms and high primary productivity there. These results indicate that control of river nutrients, especially NH_4 loading, is essential to management efforts to restore the river/estuary to a productive condition.

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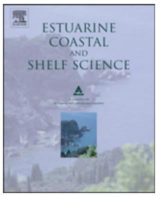

The effect of inorganic nitrogen speciation on primary production in the San Francisco Estuary

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We describe the results of a series of 96-h enclosure experiments conducted using water from stations in the northern San Francisco Estuary (SFE) along a gradient in ammonium (NH_4) and nitrate (NO_3) concentrations. Using dual-labeled $^{13}C/^{15}N$ tracers, we followed the timing and sequence of primary (carbon, C) production and phytoplankton nitrogen (N) use during experimental phytoplankton blooms. Our results show that diatoms consistently drive the phytoplankton blooms in the enclosures. By tracing both C and N uptake we provide clear evidence that high rates of C uptake are linked to phytoplankton NO_3, and not NH_4, use. Results from kinetics experiments demonstrated higher specific uptake rates (V_{MAx}) for NO_3 compared to NH_4 in the SFE. Finally, dissolved inorganic carbon and nutrient drawdown ratios in the enclosures from the chronically high NH_4 regions of the SFE were substantially lower than predicted from the Redfield ratio, suggesting suppressed C uptake, in relation to other elemental uptake. Our conceptual model of the DIN interactions that lead to higher primary production and phytoplankton blooms in the SFE suggests that higher rates of primary production that accompany phytoplankton NO_3 uptake are sufficient to outpace phytoplankton losses, leading to blooms, compared to the lower rates associated with NH_4 uptake (only 20% of that based upon NO_3). Historical changes in wastewater practices have increased the proportion of NH_4 to the DIN pool in the SFE leading to reduced access to NO_3 by phytoplankton. This may help to explain some of the reduced primary production and phytoplankton biomass observed there since the 1970s.

1. Introduction

The San Francisco Estuary (SFE) is the major west coast estuary of the U.S. and like many large estuaries worldwide has been modified as a result of urbanization (Nichols et al., 1986). Among the many manifestations of population growth and development are the diversion of freshwater from the Sacramento and San Joaquin Rivers that feed the SFE to California's Central Valley for agriculture and to southern California's urban centers (Nichols et al., 1986), ballast water introductions of invasive species (Cohen and Carlton, 1998), and nutrient loading from agricultural and municipal wastewater sources (Nichols et al., 1986; Hager and Schemel, 1996; Jassby, 2008). In recent decades declines in phytoplankton (Jassby et al., 2002) and zooplankton (Orsi and Mecum, 1996; Kimmerer and Orsi, 1996; Kimmerer, 2005) have been observed and since the early 2000's several fish, including state and federally threatened species, have also declined (Feyrer et al., 2007). These changes have led to local concern that the estuary is experiencing a "pelagic organism decline" (POD) (Sommer et al., 2007).

Historically, primary production was low in the SFE compared to other estuaries (Boynton et al., 1982; Cloern, 2001), due to high suspended sediment loads resulting in reduced photic zone depth (Cole and Cloern, 1984, 1987; Alpine and Cloern, 1988). A decline to now chronically low chlorophyll-*a* (chl-*a*) concentrations occurred in the northern SFE in the late 1980s and was attributed mainly to grazing by the overbite clam, *Corbula amurensis* (Carlton et al., 1990), which was introduced to the estuary in 1986 (Alpine and Cloern, 1992). However, *C. amurensis* abundance alone may be insufficient to explain annual chl-*a* trends, as winter chl-*a* in the northern estuary began to decline before the clam's introduction (Jassby et al., 2002) and rare spring phytoplankton blooms have been observed in the northern SFE (Dugdale et al., submitted; Wilkerson et al., 2006; Glibert et al., 2011; Dugdale et al., submitted) since the clam's introduction even while clam biomass has been relatively stable.

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Until recently (Wilkerson et al., 2006; Dugdale et al., 2007) nutrients were eliminated as a factor in the low primary production condition in the SFE as they are always found in sufficient supply (Hager and Schemel, 1996; Jassby et al., 2002). Wilkerson et al. (2006) and Hogue et al. (2005) made the first direct measurements of phytoplankton nitrogen productivity in SFE using ^{15}N tracers and found that ammonium (NH_4) fueled primary production much of the time even though high nitrate (NO_3) was present. This has been described for other estuaries (e.g. Pennock, 1987) and is explained by NH_4 inhibition of phytoplankton NO_3 uptake (e.g. Conway, 1977; Dortch, 1990). Wilkerson et al. (2006) noted an exception to the dominance of phytoplankton NH_4 uptake during spring phytoplankton blooms when phytoplankton displayed high rates of NO_3 uptake allowing the larger pool of dissolved inorganic nitrogen (DIN) to be used for growth and chl-*a* accumulation. This occurred only under conditions of low NH_4. Biomass-specific NO_3 uptake rates during these periods were the highest phytoplankton N uptake observed in the estuary during the annual productivity cycle.

A limitation of the Wilkerson et al. (2006) study is that the authors considered phytoplankton N uptake only and did not measure primary production directly as C uptake or dissolved inorganic carbon (DIC) drawdown. To estimate C production the authors assumed a fixed C to N uptake ratio (i.e. Redfield stoichiometry; Redfield et al., 1963) or used chl-*a* biomass as a proxy of phytoplankton C biomass. These assumptions may not hold as C and N uptake have been shown to be uncoupled on shorter time scales in response to perturbations in light and time of day (Cochlan et al., 1991), nutrient concentrations (e.g. surge uptake; Harrison et al., 1977), and nutrient availability. Parker (2004) reported low C uptake in Delaware Bay enclosure experiments when the N nutrient supplied was NH_4. Yoshiyama and Sharp (2006) attributed a low productivity zone in the Delaware River to high ambient NH_4 concentrations.

To establish if the speciation of ambient DIN may result in differences in carbon uptake in the SFE (i.e. a secondary bottom-up control) we conducted enclosure experiments along a natural gradient of DIN concentrations with varying NO_3 to NH_4 ratios. The goal of this study was to link phytoplankton C and N uptake processes to more fully characterize productivity – nutrient dynamics along the DIN gradient by measuring carbon uptake and DIC use directly. We hypothesize that phytoplankton in the northern SFE show a physiological advantage to growth supported by NO_3 such that higher C uptake and biomass accumulation are linked with NO_3 uptake. Observed low rates of primary production in the northern SFE may be exacerbated by a lack of access to the high ambient concentrations of NO_3 as a result of suppression of NO_3 uptake by increased anthropogenic NH_4 supply.

2. Methods and materials

2.1. Experimental design

A series of enclosure experiments were conducted in the northern SFE during 2005. Experiments were designed specifically to remove light limitation by exposing phytoplankton to 50% of surface photosynthetically active radiation (PAR) (Lorenzi, 2006) and eliminate benthic grazing by *C. amurensis*. No attempt was made to remove zooplankton grazers. Water for enclosures was collected at three stations during March, July and September. Stations were selected to represent the three subembayments of the northern estuary, Suisun (SUI; 38°2.1′ N, 122° 5.8′ W), San Pablo (SPO; 38°1.7′ N, 122° 22.2′ W), and Central Bays (CEN; 37° 53.8′ N, 122° 25.5′ W) (Fig. 1). We relied on differences in initial ambient concentrations of NO_3 and NH_4 at the three stations to create experimental treatment conditions (Table 1).

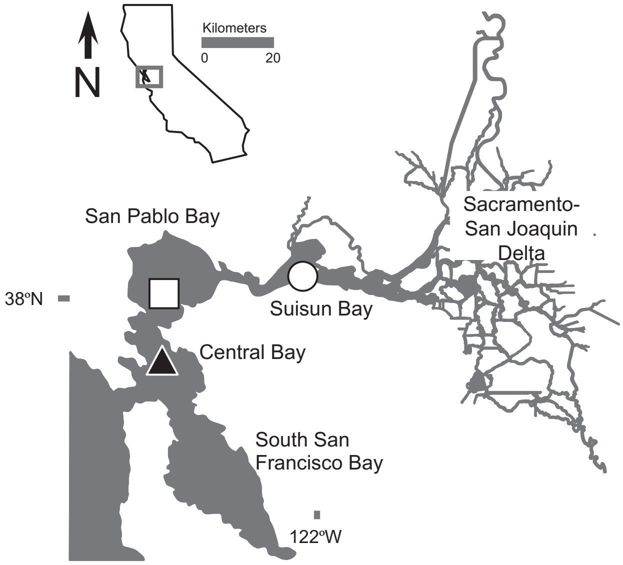

Fig. 1. Map of study site, indicating the sampling locations within the three subembayments of the northern San Francisco Bay.

Near-surface water ($<1^\circ$m depth) was collected by clean bucket at each station and dispensed into three replicate 20-L low density polyethylene (LDPE) cubitainers (=enclosures), stored in the dark in coolers, and returned to the laboratory within 2 h of collection. Temperature and salinity were measured using a YSI 85 conductivity/temperature probe (Yellow Springs Instruments, Inc.). The enclosures were placed in baywater-cooled incubation tanks with surface photosynthetically active radiation (PAR) reduced by 50% with window screening and incubated for up to 96 h. Water flow within the incubation tanks was sufficient to keep the enclosures in gentle motion during the incubation period, homogenizing the light field experienced by replicate enclosures and allowing continuous mixing with little discernable accumulation of organic matter inside enclosure walls. The nine enclosures were sampled once daily around 10:00 h local time to track changes in DIC and inorganic nutrient concentrations. Phytoplankton were assessed daily by sampling for size-fractionated chl-*a* into two fractions (GF/F 0.7 μm nominal pore size and 5.0 μm polycarbonate filters). Primary production (C uptake) and phytoplankton NO_3 and NH_4 uptake were measured daily using stable isotope tracer techniques (Slawyk et al., 1977). Phytoplankton urea uptake was measured during one enclosure experiment conducted in April 2006, representing at most 20% of NO_3 uptake (data not shown).

Water was also collected in April 2005 at CEN to study phytoplankton N uptake kinetics. After collection, water was held for 48-h at 50% PAR to allow phytoplankton to reduce the ambient N concentration prior to studying phytoplankton N uptake with increasing NH_4 or NO_3 concentrations. After 48-h, NH_4 was reduced to <1 μmol N L^{-1}. However, ambient NO_3 concentrations were still too high (>12 μmol NO_3 L^{-1}) to be able to carry out Michaelis–Menten type kinetics experiments. Consequently, additions of NO_3 were made to a series of bottles in order to determine V_{MAx} NO_3 at NO_3 concentrations in excess of 12 μmol L^{-1}.

2.2. Routine analytical methods

DIC was measured in 20-ml samples using a Monterey Bay Research Institute-clone DIC analyzer with acid-sparging and non-

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Table 1
Hydrographic data and initial chemistry at stations in Suisun Bay (SUI), San Pablo Bay (SPO) and Central Bay (CEN) during 2005. Temperature and salinity data were not determined (NA) in SUI and SPO stations in September.

Experiment	Station	Sal. (psu)	Temp. (°C)	NO_3 µmol N L^{-1}	NH_4 µmol N L^{-1}	Urea µmol N L^{-1}	PO_4 µmol P L^{-1}	$Si(OH)_4$ µmol Si L^{-1}	Chl-*a* µg L^{-1}	Chl-*a* % >5-µm
March	SUI	2.7	15.4	39.43	9.18	1.93	1.76	281	1.3	70
	SPO	15.3	15.6	35.12	5.71	1.81	1.61	165	2.4	71
	CEN	19.4	15.2	31.37	4.91	1.57	1.55	128	1.9	79
July	SUI	7.2	20.0	22.60	8.61	1.18	2.92	182	0.9	33
	SPO	17.8	19.5	21.51	5.54	1.19	3.12	115	1.0	60
	CEN	24.1	18.4	17.30	5.21	0.82	2.58	69	1.5	33
September	SUI	NA	NA	23.99	5.65	0.76	3.00	182	1.9	48
	SPO	NA	NA	18.58	5.25	1.00	3.19	105	2.3	56
	CEN	NA	16.4	15.41	4.60	0.90	2.94	80	2.0	60

dispersive infrared (NDIR) analysis (Friederich et al., 2002; Parker et al., 2006) following preservation with 200 µL of 5% w/v $HgCl_2$ (Sharp et al., 2009).

Samples for inorganic nutrients were passed through a GF/F filter to remove particulate matter before nutrient analysis (Wilkerson et al., 2006). Twenty-ml filtered water samples were analyzed using a Bran and Luebbe AutoAnalyzer II with MT-19 manifold chemistry module for $NO_3 + NO_2$ and NO_2 according to Whitledge et al. (1981) and Bran and Leubbe (1999a,b) Method G-172-96, phosphate (PO_4) according to Bran and Luebbe Method G-175-96 and silicate ($Si(OH)_4$) by Bran and Luebbe Method G-177-96. $NO_3 + NO_2$ is referred to as NO_3 throughout the text as NO_2 concentrations were very low (<1.0 µmol L^{-1}). Urea concentrations were measured in all experiments using the method of Revilla et al. (2005) with concentrations rarely exceeding 1 µmol L^{-1} (representing <3% of the DIN pool). Separate 25-ml samples were collected for manual colorimetric determination of NH_4 according to Solorzano (1969) using a 10-cm path length cell. Sample water (50-ml–100-ml) was filtered for determination of *in vitro* chl-*a* using the extraction protocol of Arar and Collins (1992) and read on a Turner Designs fluorometer calibrated with commercially available chl-*a* (Turner Designs).

2.3. Carbon and nitrogen assimilation

Dual-labeled $^{13}C/^{15}N$ stable isotope tracer incubations were carried out to estimate hourly C and N uptake rates (Slawyk et al., 1977). Trace additions of $NaH^{13}CO_3$ and either $K^{15}NO_3$ or $^{15}NH_4Cl$ (99 atom %) were added to samples to approximately 10% of the ambient concentration. Samples were incubated in 180-ml polycarbonate bottles for 4-h around local noon, held in baywater-cooled incubator tables screened to 50% of surface PAR. Incubations were terminated by gentle vacuum filtration onto pre-combusted (450 °C for 4 h) 25-mm Whatman GF/F filters. Filters were frozen until analysis for ^{13}C and ^{15}N enrichment and particulate organic carbon and nitrogen concentration with a Europa 20/20 isotope ratio-mass spectrometer system. Nitrogen uptake rates (ρ, µmol L^{-1} h^{-1}) and biomass-specific uptake (V, h^{-1}) were calculated according to Dugdale and Wilkerson (1986). Carbon uptake was calculated in the same manner, using measured DIC concentrations to calculate substrate enrichment (Legendre and Gosselin, 1996; Parker, 2005). We report both V and ρ because while the two rates are related (ρ is derived from V), V provides an indication of phytoplankton physiology, while ρ provides information on C and N flux and cycling. The particulate carbon and nitrogen retained on GF/F filters likely contained particle-associated and some fraction of free-living heterotrophic bacteria (Hoch and Kirchman, 1995). Recent measurements suggest that between 76 and 90% of bacteria in the northern SFE are free-living minimizing their contribution to the organic matter captured on the filters (Parker, Unpublished data). Because of the potential for bias in V due to detrital particulate N (Garside, 1991), specific C and N uptake were also estimated by normalizing uptake rates to chl-*a* and cells L^{-1} (Kudela et al., 1997) and showed the same trends as the traditional measure of V, normalized to PON. We report here V, normalized to PON to be consistent with previous work in the SFE (i.e. Hogue et al., 2005; Wilkerson et al., 2006; Dugdale et al., 2007). An *f*-ratio was calculated as $\rho NO_3/(\rho NO_3 + \rho NH_4)$ to evaluate the relative importance of NO_3 uptake in phytoplankton N uptake.

No correction for NH_4 regeneration and isotope dilution was made. This may result in underestimation of NH_4 uptake. However, by keeping incubation times to 4-h we have lessened the importance of NH_4 regeneration (LaRoche, 1983). In addition, the high NH_4 (ca. 10 µmol N L^{-1}) conditions and relatively low ρNH_4 (ca. 0.10 µmol N L^{-1} h^{-1}) characteristic of the northern SFE (Wilkerson et al., 2006; Dugdale et al., 2007; Parker et al., 2012) all minimize the potential impact of NH_4 regeneration on isotope dilution. Assuming an initial ^{15}N isotopic enrichment of 10% and NH_4 regeneration equivalent to uptake (0.1 µmol N L^{-1} h^{-1}) the isotope enrichment would be reduced to 9.80% after 4-h resulting in an understate of NH_4 uptake by 2% (Dugdale and Wilkerson, 1986).

3. Results

3.1. Conditions in the embayments at time of sampling for enclosures

Salinity increased moving from SUI to SPO and CEN while water temperature was similar between locations, varying by ≤0.4 °C in March and 1.6 °C in July (Table 1). Initial nutrient and chl-*a* concentrations revealed a gradient in conditions from SUI to SPO and CEN (Table 1) with the highest inorganic nitrogen concentrations found always at SUI compared to other locations. The greatest difference in initial NO_3 and NH_4 concentrations between SUI and the other stations occurred in March. During July and September NO_3 and NH_4 concentrations in the stations were more similar but with the same trends of decreasing concentrations in the seaward direction. Initial urea concentrations were <2 µmol N L^{-1} with higher urea measured in March compared to July and September. PO_4 concentrations increased from March to September with no consistent spatial pattern. In contrast, $Si(OH)_4$ was highest in March compared to July and September and consistently declined in the seaward direction during each sampling date. Chl-*a* concentrations were similar between stations during each sampling date but consistently lowest at SUI (Table 1). The absolute differences in initial chl-*a* between stations for a given sampling date were ≤1.1 µg L^{-1}. The percentage of chl-*a* in cells >5-µm varied systematically by date but not location. The majority of chl-*a* was found in cells >5 µm during March whereas during July, smaller sized cells (<5-µm) accounted for as much as 70% of the initial chl-*a* in SUI and CEN. Chl-*a* was most evenly divided between cells <5-µm and >5-µm in September (Table 1).

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3.2. Enclosure experiments: dissolved inorganic carbon, chlorophyll and inorganic nitrogen concentrations

During the enclosure time series chl-*a* increased and was always greatest in enclosures collected at SPO and CEN compared to SUI for the first 72 h (Fig. 2A) with the absolute chl-*a* concentrations highest in March compared to July and September. In each experiment the maximum chl-*a* in CEN enclosures was always observed at 72-h and began to decline by 96-h, likely in response to nutrient exhaustion (Fig. 3 shows March data). Chl-*a* in SPO enclosures continued to increase throughout the 96-h incubation period, while SUI enclosures consistently lagged SPO and CEN enclosures with no significant increases in chl-*a* during the initial 48-h. Common to all enclosures, the chl-*a* produced was mostly in the >5-μm size fraction (% >5 μm; ca. 72–100%; Table 2). The decrease in dissolved inorganic carbon concentrations in SPO and CEN enclosures (Fig. 2B, Table 2) was substantially greater than in SUI enclosures during all experiments. For example, the decrease in DIC concentration was 5- and 6-fold greater in CEN and SPO enclosures, respectively, compared to SUI during March (Fig. 2B, Table 2). The larger drawdown of DIC in SPO and CEN suggests that higher primary production was occurring in those enclosures compared to SUI.

Nutrients declined less in SUI than SPO and CEN enclosures during the 96-h incubation period (Fig. 3, Table 2). In each of the experiments NH_4 concentrations in SPO and CEN enclosures declined within the first 24-h and were reduced to < 1 μmol N L^{-1} within 48-h (Fig. 3A for March, Table 3). In contrast, NH_4 concentrations in SUI enclosures required 72-h to reach <1 μmol N L^{-1} in March and September and 96-h in July (Table 3). NO_3 concentrations began to decrease in SPO and CEN enclosures during the first 24-h in March (Fig. 3B) and within 48-h in July and September (data not shown); NO_3 exhaustion occurred by 96-h in these enclosures (Table 3). NO_3 in SUI enclosures remained largely unchanged for 72-h in March (Fig. 3B) and July and declined by 1 μmol N L^{-1}–4 μmol N L^{-1} by 96-h (Table 3). During September, NO_3 in SUI enclosures decreased by $\sim$5 μmol L^{-1} by 72-h (data not shown) with a further decline by 96-h.NO_3 was never exhausted in any of the SUI enclosures (Table 3).

Nutrient drawdown ratios, based on the disappearance of nutrients over the 96-h incubation period, show major deviations from the Redfield ratio for SUI enclosures (Table 2). C:N drawdown ratios in SUI were 3.7, 3.7 and 4.3 for March, July, and September, respectively. In contrast, C:N ratios in CEN were 6.7, 10.8, and 10.6 and in SPO were 5.5, 8.2, and 7.5. N and $Si(OH)_4$ drawdown was similar (i.e. N:Si $\approx$ 1) in all enclosures during March, in CEN enclosures in July, and SPO and CEN in September (Table 2).

3.3. Enclosure experiments: carbon and nitrogen uptake

Carbon uptake (V_C, h^{-1} and ρC, μmol C L^{-1} h^{-1}) supports the patterns observed for chl-*a* increase and DIC decrease in enclosures, with SUI enclosures revealing lower carbon uptake compared to SPO and CEN (Fig 2, Figs. 3C, D, Table 3). During March, both V_c and ρC showed little change in the first 24-h and then increased in SPO and CEN by 48-h, reaching maximal values at 72-h (Fig. 3C, D, Table 3). The maximum C uptake in SUI enclosure represented $\sim$30% of the maximum value at SPO and CEN (Fig. 3C,D). Similarly, in July, C uptake in SPO and CEN enclosures increased after 48-h and peaked at 96-h. C uptake in SUI enclosures lagged SPO and CEN by 24-h (Table 3). During September, C uptake in excess of 4 μmol C L^{-1} h^{-1} were observed in enclosures from all three bays by 48-h (data not shown). However, the maximum V_C and ρC in SUI enclosures was lower than that observed in SPO and CEN enclosures (Table 3) Overall, the time series of C uptake that was observed in the enclosures (Fig. 3C, D) resembled the pattern observed for NO_3 uptake rather than NH_4 uptake (Fig. 3E, F, G, H).

Phytoplankton N uptake was dominated initially by NH_4 uptake followed by NO_3 uptake in all enclosure experiments (e.g. March time series, Fig. 3E, F, G, H). During March, VNH_4 reached maxima within 24 h in SPO and CEN enclosures and ca.72-h in SUI (Fig. 3G). Although the time of peak VNH_4 (V_{MAx} NH_4) in SUI enclosures was

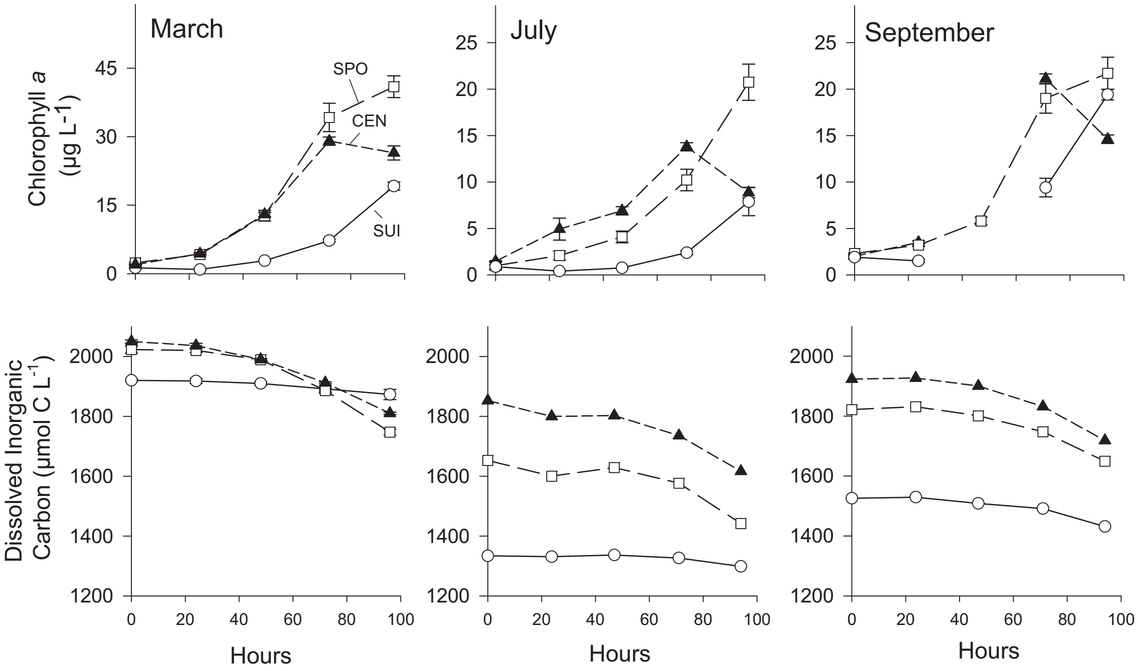

Fig. 2. Time series of chl-*a* and dissolved inorganic carbon concentrations in enclosure experiments from Suisun Bay (open circles), San Pablo Bay (open squares) and Central Bay (closed triangles) during March, July and September. Error bars represent one standard deviation based on three replicate 20-L enclosures. Note different *y*-axis scale for chl-*a* for March experiment.

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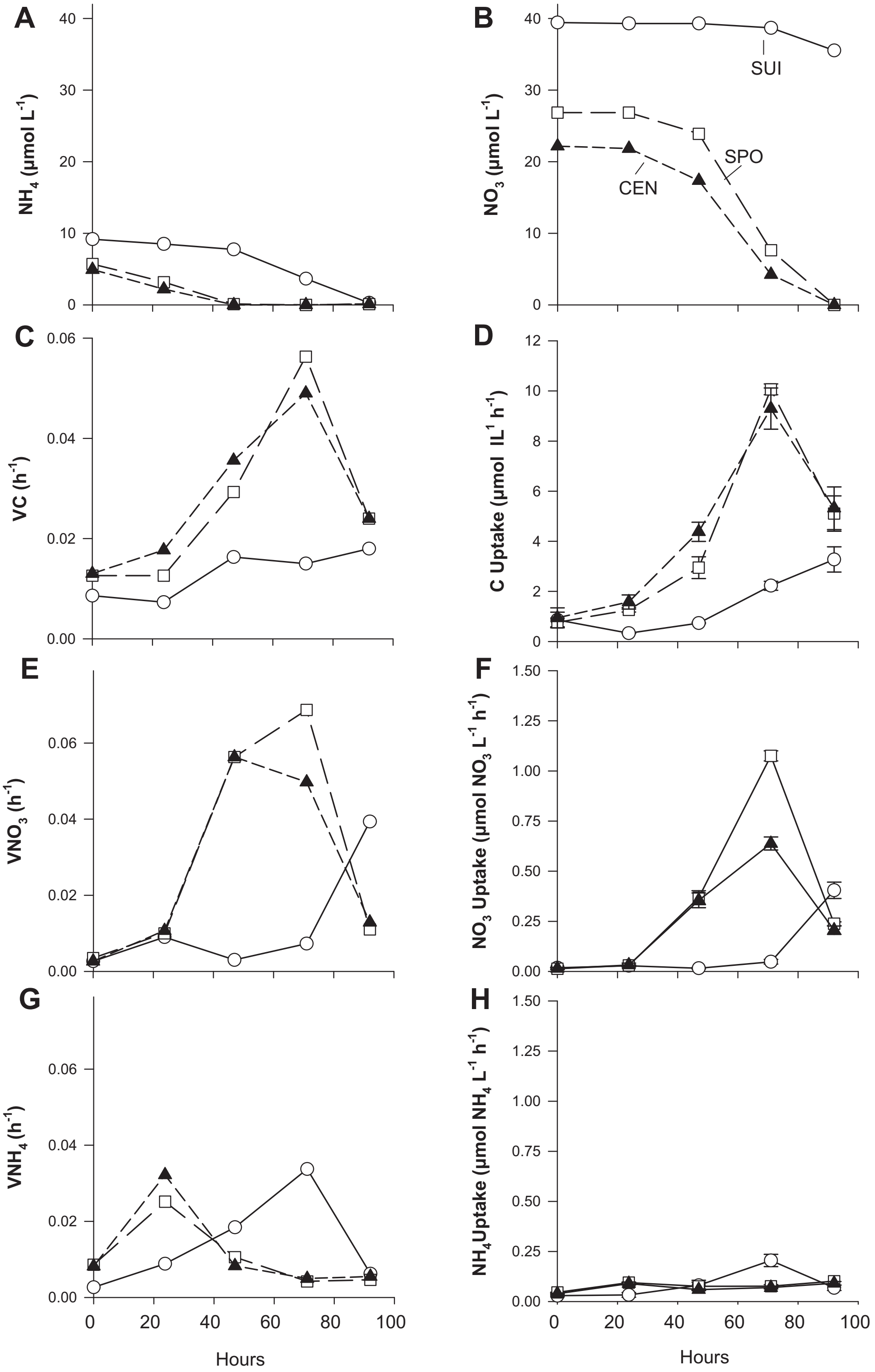

Fig. 3. Time series of NH_4 and NO_3 concentrations, specific uptake, and transport rates during 4-h daily incubations for C, NH_4 and NO_3 during March enclosure experiments conducted in Suisun Bay (open circles), San Pablo Bay (open squares) and Central Bay (closed triangles). A) NH_4, B) NO_3, C) specific C uptake, V_C, D) C uptake rate, ρC, E) specific NO_3 uptake, VNO_3, F) NO_3 uptake rate, ρNO_3, G) specific NH_4 uptake rate, VNH_4, H) NH_4 uptake rate, ρNH_4.

always 1–2 days later than in CEN or SPO enclosures, the V_{MAx} NH_4 values were similar to those of CEN and SPO in the three experiments (0.025–0.46 h^{-1}) (Table 3). ρNH_4 was low in both March (Fig. 3H) and July (Table 3) but higher in September. There was essentially no measurable NO_3 uptake in CEN and SPO enclosures for the first 24-h but a rapid increase in both VNO_3 and ρNO_3 was observed at 48-h (matching the increase in C uptake), reaching maximal ρNO_3 by 72-h (Fig. 3F, Table 3). ρNO_3 in SUI enclosures remained low up to 72-h, and only increased at 96-h. V_{MAx} NO_3 was almost always greater than V_{MAx} NH_4, often by a factor of >2

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Table 2

Elemental drawdown of dissolved inorganic carbon (DIC), dissolved inorganic nitrogen (DIN, NO_3 and NH_4), phosphate and silicate reported as total change in nutrient concentrations over 86–90-hr. Ratios of ΔC: ΔN: ΔP: ΔSi are shown normalized to P. In March PO_4 and NH_4 concentrations were exhausted by 72-hr in SPO and CEN enclosures (*); elemental drawdown ratios are given based on 72-hrs in these cases. %Chl-a >5 is the percentage of chl-*a* that was measured in cells >5-μm in diameter after 96-hr.

Experiment	Element (μmol L^{-1})	SUI	SPO	CEN
March	ΔDIC	47	270	240
	ΔDIN	12.8	48.51	36.16
	ΔP	0.74	1.61*	1.55*
	ΔSi	10.89	33.24	26.59
	C:N:P:Si	63:17:1:15	167:30:1:21	154:23:1:17
	C:N	3.7:1	5.5:1	6.7:1
	%DIN uptake as NH_4	72	12	12
	%Chl-*a* >5-μm	90	100	81
July	ΔDIC	35	211	236
	ΔDIN	9.39	26.92	22.42
	ΔP	0.75	2	1.82
	ΔSi	0.58	4.3	NA
	C:N:P:Si	46:12.5:1:1	106:13:1:2.2	129:12:1:NA
	C:N	3.7:1	8.2	10.8
	%DIN uptake as NH_4	92	21	23
	%Chl-*a* >5-μm	100	72	100
September	ΔDIC	94	172	205
	ΔDIN	22.07	23.64	19.74
	ΔP	1.43	1.91	1.93
	ΔSi	5.96	16.29	15.84
	C:N:P:Si	65:15:1:4	90:12:1:9	106:10:1:8
	C:N	4.3	7.5	10.6
	%DIN uptake as NH_4	26	22	23
	%Chl-*a* >5-μm	89	88	79

(Table 3). The exception to this was in SUI enclosures where phytoplankton had little access to NO_3 due to the high NH_4. In these cases V_{MAx} for NO_3 and NH_4 were comparable (Table 3).

3.4. *Uptake kinetics*

VNH_4 versus NH_4 concentration showed a hyperbolic relationship, with K_s for NH_4 of 1.3 μmol L^{-1} and V_{MAx} of 0.033 ± 0.003 h^{-1} (Fig. 4). Because ambient NO_3 was not reduced <12 μmol L^{-1}, we were unable to fit a Michaelis–Menten type curve or derive K for NO_3. However, saturating NO_3 uptake was V_{MAx} at 0.044 ± 0.002 (±sd) h^{-1} over a range of NO_3 from 12 μmol N L^{-1} to 35 μmol N L^{-1}. The difference in V_{MAx} for NO_3 represented ~33% increase over the V_{MAx} than achieved for NH_4.

4. Discussion

The maximum primary production reported here for enclosures are higher than rates reported previously for the northern SFE (Cole and Cloern, 1984; Kimmerer et al., 2012) reflecting the fact that light limitation was eliminated through the experimental design. The sequence of phytoplankton nutrient use and patterns of phytoplankton C and N uptake described here likely reflect periods in the estuary when light limitation is eliminated through vertical stratification of the water column. Higher C and N uptake were measured in Central and San Pablo Bays compared to Suisun Bay. Our hypothesis that phytoplankton populations in the northern SFE show a physiological advantage to growth when they use NO_3 is supported by these findings as all experiments showed elevated phytoplankton C uptake and chl-*a* accumulation associated with phytoplankton NO_3 use. Even allowing for possible isotope dilution and an underestimation of NH_4 uptake, maximum NO_3 uptake rates were consistently higher than maximum phytoplankton NH_4 uptake rates, ensuring effective use of the high ambient NO_3 concentrations in the northern SFE.

Three lines of evidence suggest that the phytoplankton group that responded most favorably to the enclosures conditions were diatoms. Results of size-fractionated chl-*a* showed that the phytoplankton community was dominated by larger cells which have been interpreted previously as diatom biomass in the SFE (Cloern

Table 3

Summary of enclosure experiments in March. July and September 2005. V_{MAx} and ρM_{Ax} (maximum V and ρ observed in the enclosure) and time to reach V_{MAx} for C, NO_3, and NH_4. Initial NO_3 and NH_4 and time to NO_3 exhaustion and NH_4 <1 μmol L^{-1} also provided.

	March			July			September		
	SUI	SPO	CEN	SUI	SPO	CEN	SUI	SPO	CEN
V_{MAx} C (h^{-1})	0.018	0.056	0.049	0.041	0.043	0.040	0.055	0.085	0.102
ρ_{MAx} C (μmol C L^{-1} h^{-1})	3.27	10.06	9.29	10.53	10.53	9.67	8.89	13.38	15.97
Time to V_{MAx} C (h)	96	72	72	96	72	72	72	48	48
Initial NO_3 (μmol N L^{-1})	39.43	35.12	31.37	22.60	21.51	17.30	23.99	18.58	15.41
Time to exhaustion, (h)	>96	96	96	>96	96	96	>96	96	96
V_{MAx} NO_3 (h^{-1})	0.039	0.069	0.056	0.041	0.046	0.075	0.030	0.088	0.116
Time to V_{MAx} NO_3 (h)	92	71	71	92	47	47	72	47	47
ρ_{MAx} NO_3 (μmol N L^{-1} h^{-1})	0.40	1.08	0.64	0.24	0.35	0.76	1.35	1.18	0.41
Initial NH_4 (μmol N L^{-1})	9.18	5.71	4.19	8.61	5.54	5.21	5.65	5.25	4.60
Time to <1 μmol L^{-1}	72	48	48	96	48	48	72	48	48
V_{MAx} NH_4 (h^{-1})	0.034	0.025	0.032	0.046	0.040	0.031	0.028	0.032	0.038
ρ_{MAx} NH_4 (μmol N L^{-1} h^{-1})	0.21	0.03	0.07	0.28	0.30	0.27	0.72	0.72	0.72

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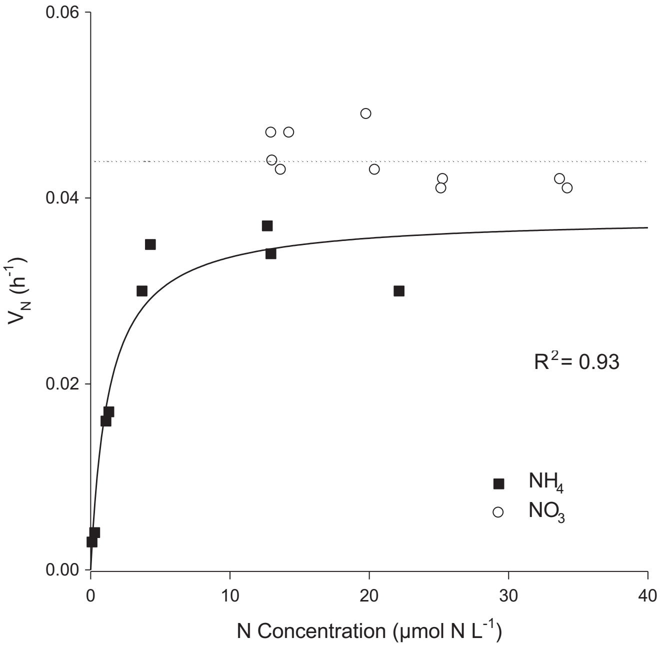

Fig. 4. Michaelis–Menten kinetic curves for NO_3 (open circles) and NH_4 (closed squares) in central San Francisco Bay in April 2005. Data for VNH_4 vs. [NH_4] were fit to a hyperbolic function. Dotted line is average V_{NO_3}.

and Dufford, 2005; Wilkerson et al., 2006). N to Si nutrient drawdown ratios approached 1:1, as would be expected if diatoms contributed significantly to phytoplankton production (Brzezinski, 1985). Limited microscopy conducted on samples from our enclosure experiments identified several diatom species including *Skeletonema costatum, Leptocylindrus minimus* and small centric diatoms making up the bulk of the phytoplankton biomass (E. Carpenter, pers. comm.). Diatom dominance in the experimental enclosures is consistent with previous field studies in the northern SFE that have shown diatom dominance during phytoplankton blooms (Dugdale et al., submitted; Cloern, 1979; Cloern and Dufford, 2005; Lidström, 2009; Dugdale et al., submitted) and as an important food source within the pelagic foodweb of the SFE (Peterson et al., 1985).

4.1. *Anomalously low phytoplankton carbon and nitrogen assimilation in Suisun Bay*

In many ways the Suisun Bay enclosures showed different responses compared to Central and San Pablo enclosures. Suisun Bay enclosures had the highest initial NH_4 and phytoplankton showed a lagged response to the improved light conditions afforded by the experimental design. The timing of the maximal phytoplankton C and NH_4 uptake and the initiation of phytoplankton NO_3 uptake and chl-*a* accumulation was delayed by at least 24-h in Suisun Bay compared to San Pablo and Central Bay enclosures. The observed lag in phytoplankton NH_4 uptake in Suisun Bay was previously unappreciated. This lag and lower rate of NH_4 uptake, together with elevated ambient NH_4 acts to further delay the initiation of phytoplankton NO_3 use and the accompanied accumulation of chl-*a*. In nature, the delay in the timing of phytoplankton bloom initiation would likely result in fewer observed blooms in Suisun Bay (Dugdale et al., 2007). The delayed NO_3 uptake and the apparent link between carbon uptake and NO_3 uptake in Suisun Bay (Fig. 3D, F) results in lower C:N drawdown ratios than would be predicted by the Redfield Ratio (Redfield et al., 1963), with DIC drawdown only 40–60% of the carbon uptake predicted based on DIN drawdown (Table 2). We interpret these anomalous responses by Suisun Bay phytoplankton to reflect some stress on growth processes. The high NH_4 condition, the result of wastewater loading to the northern SFE (Jassby, 2008), is potentially exacerbated by some additional stress that results in low NH_4 uptake rates. Owing to its proximity to the Sacramento/San Joaquin Delta, which receives nearly half of California's surface water, there are a large number of potential contaminants including herbicides and pesticides (Kuivila and Hladik, 2008; Weston and Lydy, 2010; Werner et al., 2010), and metals (Johnson et al., 2010).

4.2. *Ammonium effects on phytoplankton production*

Investigators working in other systems have suggested that anthropogenic NH_4 concentration above some value may inhibit phytoplankton primary production. MacIsaac et al. (1979) investigated the effect of sewage effluent on coastal productivity and found that at >20 μmol NH_4 L^{-1}, C uptake was depressed, resulting in C:N uptake ratios of 2:1–3:1, similar to what was observed here for enclosures from Suisun Bay. Yoshiyama and Sharp (2006) examined a 26-yr dataset form the Delaware estuary and observed a "striking decline in production at NH_4 levels above a low threshold (10 μmol L^{-1}) suggesting a strongly negative influence of NH_4 itself, or something that accompanies high NH_4 concentrations, or both". Depression of primary production and phytoplankton NH_4 uptake was recently reported for the Sacramento River, immediately downstream of the Sacramento Regional Wastewater Treatment Plant (SRWTP) (Parker et al., 2012). Suisun Bay chronically experiences high ambient NH_4 concentrations with 90% of NH_4 in Suisun Bay originating at the SRWTP (Jassby, 2008). During the three year time series of Wilkerson et al. (2006) only one phytoplankton bloom with chl-*a* >30 μg L^{-1} was observed in Suisun Bay that occurred during a period of anomalously low NH_4 and substantial phytoplankton NO_3 uptake. Similarly, Dugdale et al. (submitted) documented two spring phytoplankton blooms in Suisun Bay during 2010 (the first known blooms in Suisun Bay since 2000), with their initiation attributed to low initial NH_4 concentrations as a result of freshwater dilution. In April 2007, we also observed a similar low NH_4 period in Suisun Bay and conducted an enclosure experiment. In this case, Suisun Bay phytoplankton dynamics followed the sequence typically observed in San Pablo and Central Bays (Fig. 5) and the phytoplankton were able to use all of the available NO_3 and accumulate chl-*a* within the 96-h incubation period. The present findings and those of Wilkerson et al. (2006) suggest that there are situations when Suisun Bay phytoplankton have the capacity to grow as well as those in Central Bay when NO_3 is made available by low NH_4 concentrations.

We observed NH_4 inhibition of NO_3 uptake in the enclosure experiments using water collected in all three embayments of the northern SFE and plotting ρNO_3 vs NH_4 concentrations (Fig. 6A, B), as seen in previous studies (Dugdale et al., 2007; their Fig. 2). We found that in the enclosure experiments with >1 μmol NH_4 L^{-1}, NO_3 uptake was relatively low and uniform. NH_4 inhibition of NO_3 uptake at low NH_4 concentrations (<1 μmol L^{-1}) has been known for some time in oceanic studies (e.g. Eppley et al., 1969; Conway, 1977) and at higher concentrations for several estuaries (e.g. Glibert et al., 1982; Pennock, 1987; Collos, 1989). While the phenomenon of NH_4 inhibition of NO_3 uptake is accepted universally, as pointed out in the review by Dortch (1990), its ubiquity in natural systems is less clear This may be particularly true in high NO_3 eutrophic systems where in some cases NO_3 uptake does not appear to be influenced by NH_4 concentration. At high NO_3 concentrations NO_3 may even inhibit phytoplankton NH_4 uptake (Dortch, 1990).

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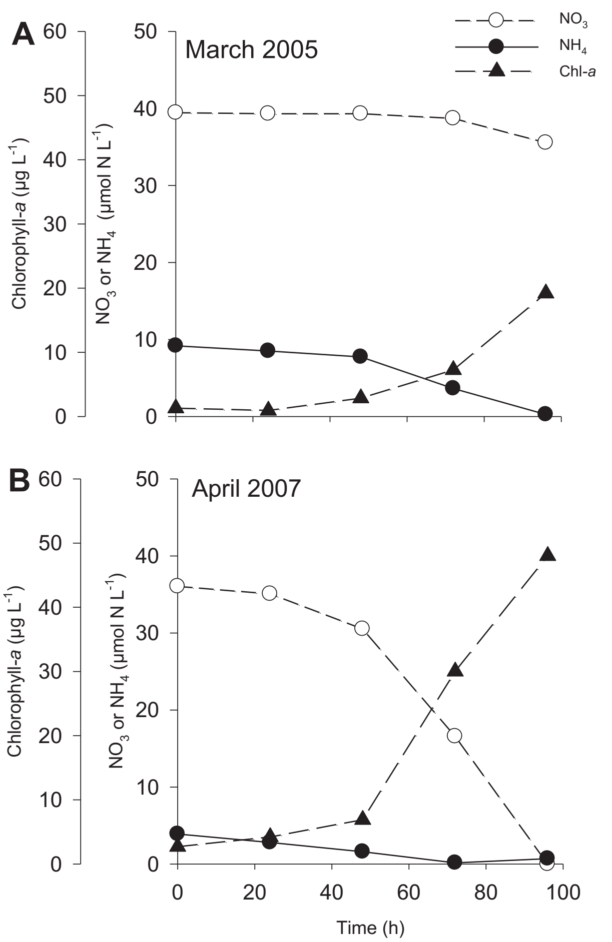

Fig. 5. NH_4, NO_3 and Chl-*a* concentrations over 96-h time series in enclosures collected at the same location in Suisun Bay during 2005 (A) and 2007 (B). Initial NH_4 concentrations in 2005 were 9.2 µmol L^{-1} and 3 µmol L^{-1} in 2007.

The sequential use of first NH_4 and then NO_3 as a result of the inhibition of phytoplankton use of NO_3 by NH_4 is often interpreted as a "preference for NH_4" (McCarthy et al., 1977). However, some phytoplankton, particularly diatoms, may display an increased capacity for NO_3 assimilation compared to NH_4 and may grow as well, or better on NO_3 (Thompson et al., 1989; Cochlan et al., 1991) and could equally be interpreted as a "preference" for NO_3 (Lomas and Gilbert, 1999a). The significance of this interaction between NH_4 and NO_3 in this study is that at low NH_4 concentrations, NO_3 uptake and high rates of primary production and chlorophyll accumulation can occur.

4.3. *Maximal NO_3 uptake exceeds maximal NH_4 uptake*

In these enclosures, as in the enclosures described in Dugdale et al. (2007) maximal rates on NO_3 uptake achieved (once NH_4 inhibition was alleviated) were always greater than those of NH_4. This may be due to different uptake kinetics with linear, not Michaelis–Menten hyperbolic, NO_3 uptake and to acceleration (or shift-up) of NO_3 but not NH_4 uptake. In this study we observed classical Michaelis–Menten kinetics for NH_4 but were unable to determine N uptake kinetics for NO_3, although comparing rates obtained with saturating level of the two DIN species, there was higher V_{MAx} for NO_3 compared to NH_4. Deviation (to linear or biphasic) from the hyperbolic relationship for NO_3 uptake at saturating to supersaturating concentrations have been described in many algal species including diatoms (Serra et al., 1978; Watt et al., 1992; Collos et al., 1992, 1997, 2005; Lomas and Glibert, 1999b) and upwelled phytoplankton (Dugdale et al., 2006). Two studies (Huntsman and Barber, 1977; Lancelot and Billen, 1985) showed that C and N uptake were coupled during linear NO_3 uptake at high concentrations. We are aware of only one study demonstrating deviations from Michaelis–Menten kinetics for NH_4 uptake, associated with the paralytic-shellfish poison-producing dinoflagellate *Alexandrium catenella* (Collos et al., 2006). Acceleration of NO_3 uptake (V_{MAx} NO_3) as a function of NO_3 concentrations (termed "shift-up") was described in recently upwelled waters (Dugdale et al., 1990) and shipboard enclosures (Wilkerson and Dugdale, 1987) with the consequence that all of the initial NO_3 was exhausted in 4–5 days, regardless of initial NO_3 concentration. V_{MAx} NH_4 uptake does not appear to accelerate linearly with NH_4 concentration. Consequently, the ratio of V_{MAx} NO_3:V_{MAx} NH_4 is variable and, as in this study, almost always >1 after 24-h to 48-h of incubation under favorable irradiance. Although the shift-up phenomenon for NO_3 uptake was originally described for the coastal ocean, it appears to also occur in estuaries, and may help to explain how the maximal uptake of NO_3 is greater than that of NH_4 in the experimental enclosures.

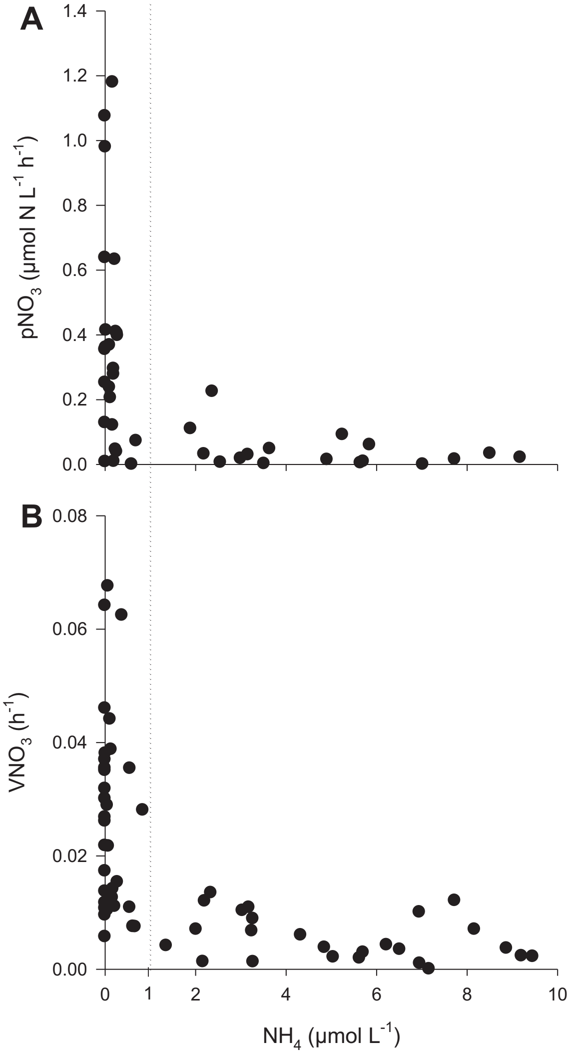

Fig. 6. A) NO_3 uptake rates versus NH_4 concentration. B) Biomass-specific NO_3 uptake versus NH_4 concentration. Results from enclosure experiments conducted in March, July and September ($n = 120$).

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4.4. Phytoplankton C Uptake and biomass accumulation linked to phytoplankton NO_3 use

Phytoplankton specific carbon uptake, normalized to either POC or chl-*a*, was higher during periods of phytoplankton NO_3 uptake compared to periods of phytoplankton NH_4 uptake (Fig. 3C, Table 3). Few published studies exist showing enhanced phytoplankton growth with NO_3 versus NH_4 (Thompson et al., 1989; Cochlan et al., 1991; Lomas and Gilbert, 1999a). Parker (Unpublished data) conducted mesocosm experiments in the Delaware Estuary in which phytoplankton were supplied with either NO_3 or NH_4 and found 2-fold higher increases in POC and chl-*a* increase in the NO_3 treatment over 56-h. Serra et al. (1978) showed that *S. costatum* growth rates were initially higher with NH_4 compared to NO_3 and NO_2 but NO_3 growth eclipsed NH_4 growth later in the experiment; the difference attributed to inducible adaptive enzymes required for NO_3 uptake (e.g. nitrate reductase).

The carbon drawdown and nutrient drawdown ratios observed in these enclosures (Table 2) show that when NH_4 is the major source of DIN being used by the phytoplankton (i.e. in SUI enclosures) C drawdown is low and the C:N drawdown ratio is roughly half of the Redfield ratio (Table 2). Conversely when both NO_3 and NH_4 are being used (as exemplified by the CEN and SPO enclosures) then the C drawdown is high and C:N drawdown approaches or exceeds the Redfield ratio. For example in March, DIC drawdown in SUI was only 17% of that observed in SPO. An NH_4 based system will likely exhibit a primary production of <20% of that where NO_3 is fully used. It is true that heterotrophic bacteria in our enclosures likely contribute to some fraction of DIN disappearance, complicating this interpretation. However, the large phytoplankton biomass in the experimental enclosures (>20 μg chl-a L^{-1}) probably far exceeds bacterial biomass and nutrient cycling processes.

4.5. An evolving conceptual model of phytoplankton bloom development in high NH_4 estuaries with Implications for management

The classical view is that phytoplankton blooms in SFE are controlled by the availability of light, with spring blooms occurring as a result of brief periods of water column stratification (Alpine and Cloern, 1988). However, anthropogenic NH_4 may play a modulating role in bloom formation by limiting access to the NO_3 pool reducing the potential for enhanced phytoplankton C and NO_3 uptake once light conditions improve. We suggest the following scenario of C, NO_3 and NH_4 uptake and phytoplankton bloom development for northern SFE (Fig. 7A). Phase 1 is characterized by low NH_4 uptake and low C uptake; there is virtually no NO_3 uptake due to NH_4 inhibition and C:N uptake ratios are low. Once NH_4 is almost exhausted, phase 2 begins with a rapid uptake of NO_3 coupled with high C uptake; C:N uptake ratios increase over this period. Finally, as NO_3 is exhausted, the system enters phase 3 of bloom development, and phytoplankton become N-limited, relying primarily on recycled NH_4 or intracellularly stored NO_3; relatively high C:N uptake ratios are observed.

Results from the Central Bay enclosure experiments completed in September (Table 3) are plotted for comparison with this conceptual model (Fig. 7B). C:N ratios calculated from ^{13}C and ^{15}N tracer results and the f-ratio are provided (Fig. 7C). C:N ratios confirm the progression from low C:N to balanced growth and finally high C:N ratios as the f-ratio increased, reflecting a greater dependence on NO_3 over NH_4 uptake. In general, phytoplankton remain in phase 1 of the scenario much of the time in the northern SFE as a result of poor light conditions and high ambient NH_4. These conditions result in low primary production and low biomass. In recent years this has prevented spring blooms occurring in Suisun Bay except twice in 2000 and 2010 when NH_4 concentrations were low (Dugdale et al. submitted; Wilkerson et al., 2006) and phytoplankton shifted to phase 2 and 3 of the bloom progression.

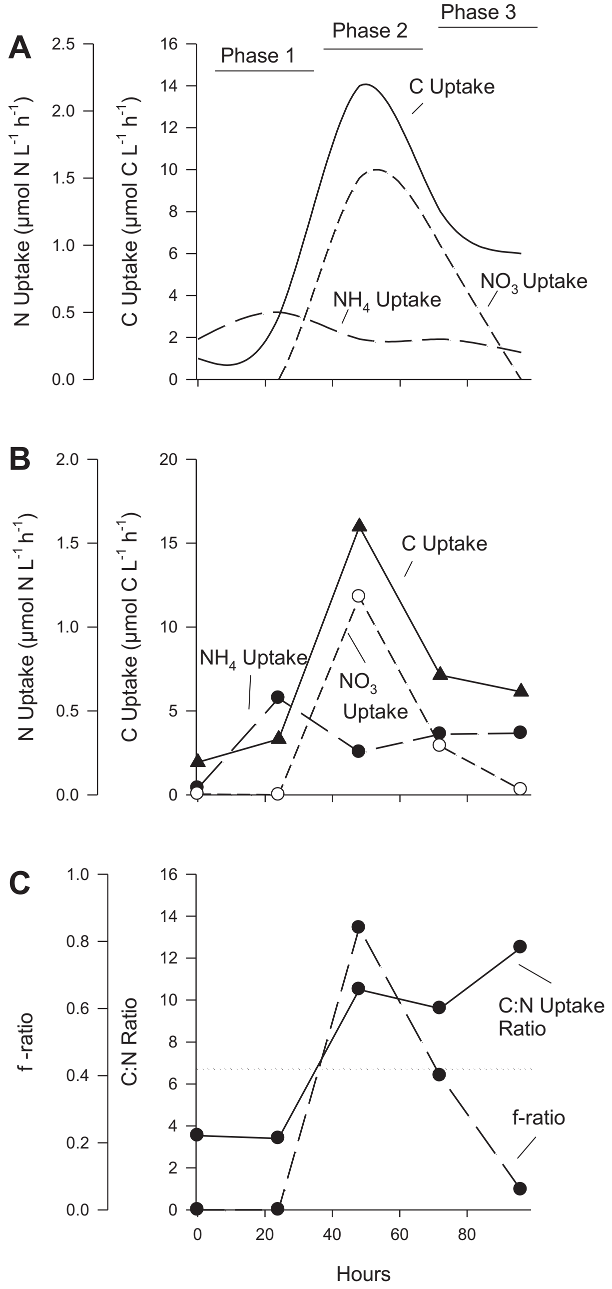

Fig. 7. A) Idealized sequence of carbon, NH_4 and NO_3 uptake in enclosure experiments. B) Data from central Bay enclosures during September. C) C:N uptake ratios and f-ratio for September.

NH_4 concentrations have steadily increased in the northern SFE since 1979 (California DWR; Jassby, 2008) as a result of human population increase; the major input of NH_4 being wastewater discharge (Hager and Schemel, 1992; Jassby, 2008). In Suisun Bay, the 4 μmol NH_4 L^{-1} threshold (Dugdale et al., 2007) for the inhibition of phytoplankton NO_3 uptake is generally exceeded during spring and summer (Jassby, 2008). We speculate that changing wastewater management practices to favor the discharge of NO_3 rather than NH_4 may increase primary production in the northern

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SFE. NO_3 stimulated primary production would likely enhance secondary production, which may be beneficial to fisheries in the Bay and nearshore (Pacific) waters. Understanding the phytoplankton response to nutrient enrichment is a major challenge to estuarine scientists and will require more sophisticated models of coastal eutrophication (i.e. Cloern, 2001; Sharp, 2001). We suggest that careful consideration of not only DIN loading but also N speciation of the DIN must also be considered for effective nutrient management strategies. As well illustrated by this study, enabling NO_3 utilization by phytoplankton will increase the rate of carbon uptake (i.e. primary production), and chl-*a*, whereas contaminant levels of NH_4 will keep carbon uptake low and may even be sufficiently toxic to decrease productivity directly.

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Technical Memorandum
Nutrient Science Summary

February 1, 2014

Historically, scientists have described primary productivity in the Bay-Delta as not being limited by nutrients (Cloern 2001; Lopez et al. 2006) and not experiencing signs of classic eutrophication (Cloern 2001). Such classic eutrophication effects include increased chlorophyll a (chl-*a*) in the water column (i.e., more algal blooms), development of hypoxia or anoxia (low or no dissolved oxygen, respectively), loss of native submerged aquatic vegetation, increased proportion of those algae that are considered harmful algal blooms (HABs), and changes in biodiversity, including loss of certain fisheries (e.g., Cloern 2001; Anderson et al. 2002). However, we now recognize that changes in nutrient loads are affecting ecosystem dynamics in complex ways that extend beyond our historic understanding of the process of eutrophication.

Nutrient effects on aquatic systems are far more complex than those normally associated with eutrophication and can occur across the full spectrum of nutrient limitation to nutrient super-saturation (Glibert et al 2013). Even relatively small changes in nutrient supply – even when those nutrients are not limiting for primary production - are being shown to have large consequences on many important properties of ecosystems (Nielsen, 2003). Two important properties of nutrient supply that have effects beginning at the level of the physiology of primary producers (algae) and propagating through the food web are the form in which nutrients are supplied (chemical state, oxidized vs. reduced, organic vs. inorganic, dissolved vs. particulate) and the proportion of different elements (including carbon (C), nitrogen (N), phosphorous (P), and silicon (Si), among others). In the Bay-Delta, the total loads, the forms, and the relative proportions of nutrients have been changing over time. These changes have had profound effects on ecosystem structure of this system, as documented below. This technical memorandum describes the effects of two such changes: the proportion of ammonium to nitrate (NH_4:NO_3) and the proportion of nitrogen to phosphorus (N:P).

Ammonium:Nitrate

For decades, researchers have explored the relative use – or relative preference for – different forms of nitrogen (N) by phytoplankton. Ammonium (NH_4) is generally considered to be the form of nitrogen preferred by phytoplankton due to the more favorable energetics associated with its assimilation compared to that of nitrate (NO_3). Ecological consequences of dependence on NO_3 vs. NH_4 have also been well recognized for decades. Based on the concept of "new" and "regenerated" production (Dugdale and Goering 1967, Eppley and Peterson 1979), phytoplankton dependence on NH_4^+ leads to production that is cycled within the microbial loop, whereas that based on NO_3^- more often leads to production that supports a food web leading to secondary production as well as export out of the euphotic zone (Dugdale and Goering, 1967; Eppley and Peterson, 1979). Shifts in nitrogen (N) form from NO_3^- to NH_4^+ have been shown in numerous systems to lead to community shifts away from plankton communities dominated by diatoms to those dominated by flagellates, cyanobacteria, and bacteria, in turn, resulting in a shift in composition of higher food webs (e.g., Legendre and Rassoulzadegan, 1995; Glibert, 1998; Mousseau, 2001; Heil et al., 2007). Until recently, most of the data illustrating such changes resulting from shifts in nutrient form were derived from systems for which N was the limiting nutrient. An important question in this context is whether the physiological and ecological consequences of dependence on NO_3^- versus NH_4^+ remain the same under nutrient rich conditions as under conditions of nutrient deficiency. A classic assumption is that when cells are growing at maximal growth rates (set by environmental conditions of light, temperature, etc.), it is fully expected that the total N taken up by cells will be the same whether they are provided NO_3^- or NH_4^+ (or urea or other forms of N). In some nutrient rich (but not classically eutrophic) estuaries receiving high loads of NH4 there is evidence for reduced, rather than increased, rates of primary productivity, compared to systems receiving comparable N loads in oxidized forms; such systems have been termed High Nutrient Low Growth (HNLG) systems (Yoshiyama and Sharp 2006).

Although nutrient effects have generally not been considered controlling factors in San Francisco Estuary, the more subtle ecological impacts of NH_4^+ loading and the importance of changes in NO_3^-:NH_4^+ in phytoplankton succession are beginning to be considered as important factors that may have contributed to historical changes seen in the food web (e.g., Dugdale et al., 2007; 2012, 2013; Glibert, 2010; 2012; Glibert et al., 2011; Parker et al., 2012a,b). Not only have dominant species changed in this system, but rates of primary production have also declined over the course of the past few decades (e.g., Jassby et al., 2002; Kimmerer et al., 2012). Without question, the Bay Delta is receiving high loads of NH_4 and these loads have increased over the recent decades (Fig. 1). A question receiving considerable attention is whether these concentrations of NH_4 have contributed to the tilting of the Bay-Delta away from a productive ecosystem to one that has HNLG characteristics. Based solely on previously reported ambient chl *a* in Suisun Bay values that tend to be <5 μg L^{-1} on average (occasional blooms excepted), combined with ambient nutrient concentrations, this system is characteristic of an HNLG region (Yoshiyama and Sharp, 2006; Dugdale et al., 2007).

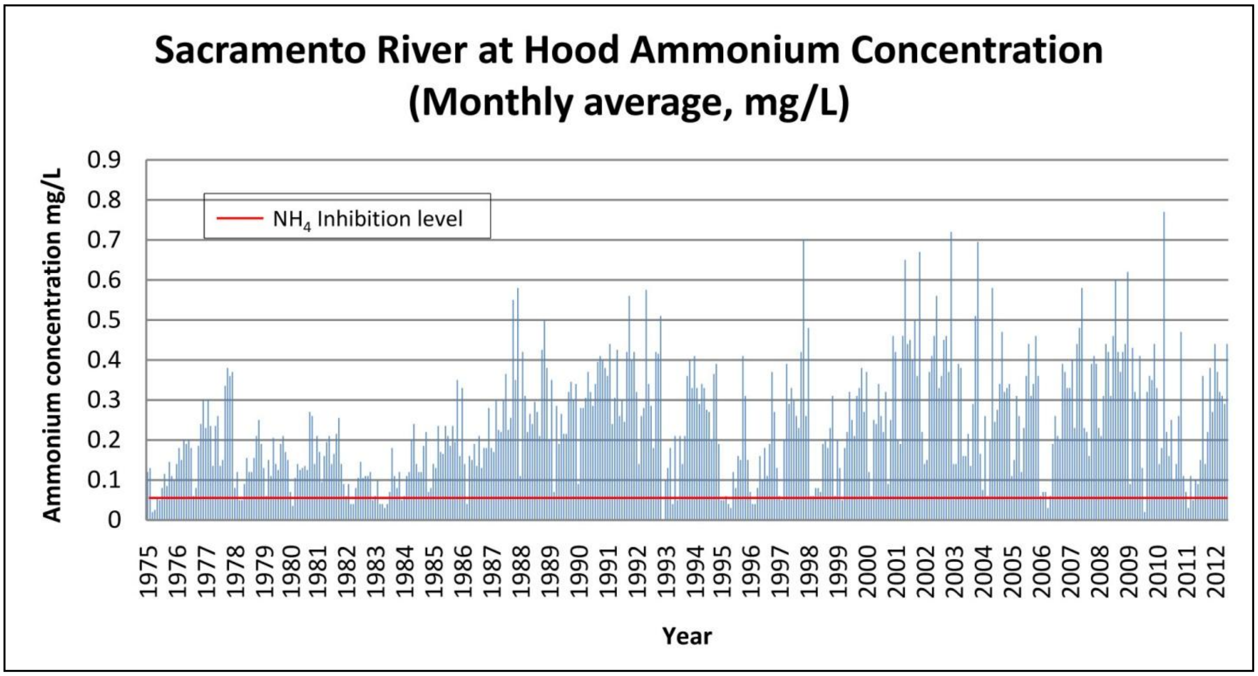

Figure 1. Average monthly ammonium concentration in the lower Sacramento River at Hood. Source: Environmental Monitoring Program data.

The fundamental mechanism contributing to HNLG systems is the inhibition of NO_3 uptake by NH_4. More correctly termed "repression" rather than "inhibition", this phenomenon is well documented throughout the physiological literature. Both NH_4^+ and NO_3^- are transported across the cell membrane by both passive and active pathways. Active pathways involve transporters, specific proteins that transport the targeted molecules. For most algal functional groups, once transported into the cell, NO_3^- is first reduced to NO_2^- through the activity of Nitrate Reductase (*NR*) and subsequently further reduced to NH_4, the form that can be assimilated into amino acids and proteins for cell growth. Both the process of NO_3^- transport into the cell and its subsequent reduction to NH_4 can be inhibited (or repressed) by NH_4. Because of differences in the physiology of transporters and cell metabolism between different classes of algae, different types of algae have different susceptibilities to NH_4^+. Such differences contribute to the confusion about, different observations of, and different interpretations as to the importance of, NH_4 in regulating productivity of algae.

The inhibition or repression of NO_3^- uptake by NH_4^+ needs to be differentiated from the metabolic effect of toxicity of NH_4^+ or NH_3. *NH_4^+ is, in fact, best characterized as a paradoxical nutrient – preferentially used at one end of the concentration spectrum when N is limiting and toxic to the cell when supplied at super-saturating levels* (Britto and Kronzucker 2002). Whereas NH_4^+ is transported across the cell membrane via active transport, the unionized form, $NH_{3,}$ can diffuse through membranes (Kleiner 1981). The presence of NH_3 increases with increased pH, a condition that is not the norm in aquatic systems, except under dense blooms. More about toxicity effects of NH_4 and NH_3 can be found in the Total Ammonia Toxicity section below.

NH_4 suppression of NO_3 uptake when both nutrients are in ample supply must also be differentiated from the preferential use of NH_4 by phytoplankton when N is limiting. Under the latter conditions, phytoplankton will use NH_4 preferentially because it requires less energy than NO_3. Under the former conditions, the cells must cope with an excess; and in doing so, their metabolism is less capable of assimilating NO_3.

The effects of changes in the proportion of NH_4:NO_3 have been shown for the Bay-Delta in both field observations and laboratory experiments. Parker et al. (2012a) observed a 60% decline in primary production in the Sacramento River below the Sacramento Regional Wastewater Treatment Plant, where NH_4 is discharged, compared to production above the Treatment Plant's outfall. Also supporting this finding, Parker et al. (2012b) found that "[b]y tracing both carbon (C) and N uptake we provide clear evidence that high rates of C uptake are linked to phytoplankton NO_3, and not NH_4, use." They conclude that the increased proportion of NH_4 "may help explain some of the reduced primary production and phytoplankton biomass observed [in the San Francisco Estuary] since the 1970s."

In enclosure experiments with samples from Central Bay, Suisun Bay, and the Sacramento River at Rio Vista, representing a gradient of both nutrient concentrations and proportions of different forms of N, Wilkerson et al. (in preparation) observed "a gradient of decreasing phytoplankton physiological rates in the upstream direction as far as Rio Vista." Phytoplankton productivity rates (both carbon and nitrogen uptake) decreased with increasing concentrations of NH_4.

In a series of recent experiments conducted with natural samples from the Sacramento River, the effects of altered proportions of NH_4:NO_3 were also apparent (Glibert et al. 2012b). In these experiments, the proportions of these nutrients were manipulated, and both short-term N uptake rates and longer-term N production rates were assessed. Two findings are of note. First, when 20 µmol NH_4 was added to the sample, a concentration commonly observed in the Sacramento River, and the rate of NO_3 uptake was measured across a concentration gradient, the rate of uptake of NO_3 decreased significantly compared to unamended rates measured over a period of < 1 hour (Figure 2). Second, when samples were enriched with NH_4, $NO_{3,}$ or urea (at the molar equivalent dose) for a period of 24-48 hours, and then rates of uptake of all N forms measured, the summed rate of N uptake in the NH_4-added treatment was significantly lower than that in the NO_3-added or urea-added treatments (Figure 3).

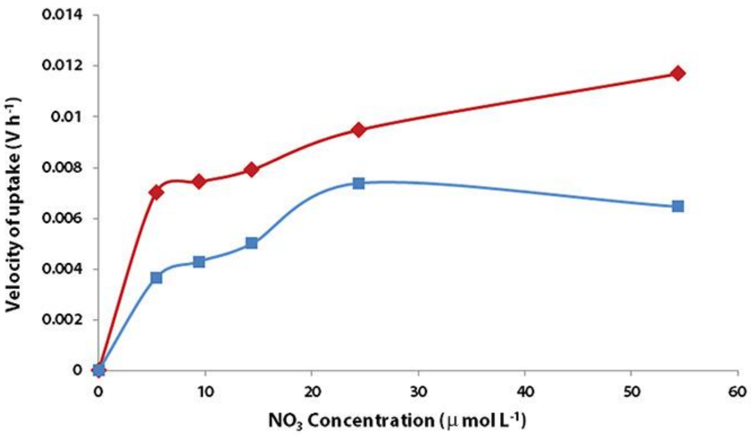

Figure 2. Velocity of uptake of NO_3 as a function of added NO_3 enrichment (red curve), and the same relationship but with a constant addition of 20 µmol L^{-1} NH_4 (blue curve). Nitrate uptake is reduced when NH_4 is added. Experiment was conducted with water collected from the Sacramento River. Data from Glibert et al. (2012b).

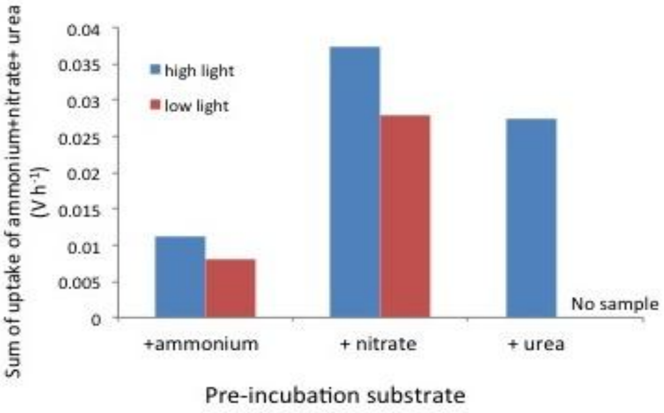

Figure 3. Summed rate of uptake of nitrate+ ammonium+ urea for samples collected from the Sacramento River and pre-incubated with the substrate indicated, after which short-term uptake rates were measured using ^{15}N tracer techniques**.** The experiment was conducted under both high (blue bars) and low (red bars) irradiance levels. The summed rate of N uptake in the NH_4-added treatment was significantly lower than that in the NO_3-added or urea-added treatments. From Glibert et al. (2012b).

Longer term responses were also found in paired experiments in which NO_3 and NH_4 concentrations were manipulated for San Francisco Bay-Delta samples collected over 2 years, leading to different types of phytoplankton developing over a period of several days of exposure. A greater response by fucoxanthin-containing organisms (diatoms) was observed in those samples enriched with NO_3^-, and greater responses by zeaxanthin and Chl *b*-containing organisms (predominantly cyanobacteria and chlorophytes) were observed in samples enriched with NH_4^+ (Glibert et al., in review). A series of 3-week nutrient-rich mesocosm experiments conducted in Wascana Lake, Saskatchewan, Canada, yielded largely similar findings: total cyanobacterial biomass was associated with NH_4^+ treatments and diatom biomass was associated with NO_3^- treatments (Donald et al., 2013). In recent experiments conducted in the tidal freshwater estuarine zone of the Guadiana Estuary (Spain and Portugal), it was also found that NO_3 consumption decreased with increasing NH_4 uptake, and these findings were most pronounced during the most productive period. Total primary productivity was suppressed as a result (Domingues et al. 2011). As stated by Domingues et al. (2011), "…increased inputs of N as NH_4 due to urban waste effluents may result in a shift in phytoplankton community composition, towards a dominance of cyanobacteria and green algae."

This finding is further supported by the 37 years of data collected by the Environmental Monitoring Program in the Bay-Delta. When monthly data of chl-a and diatom cell count are plotted against NH_4 levels for the period 1975 to 2012 there is a marked decreasing trend in both as ammonium levels rise, with an increasing effect around the 0.056 mg L^{-1} (4 µmol L^{-1}) level (Figures 4 and 5). This level of NH_4 has been identified as a threshold value above which inhibition or repression of NO_3 uptake begins (Dugdale et al. 2007).

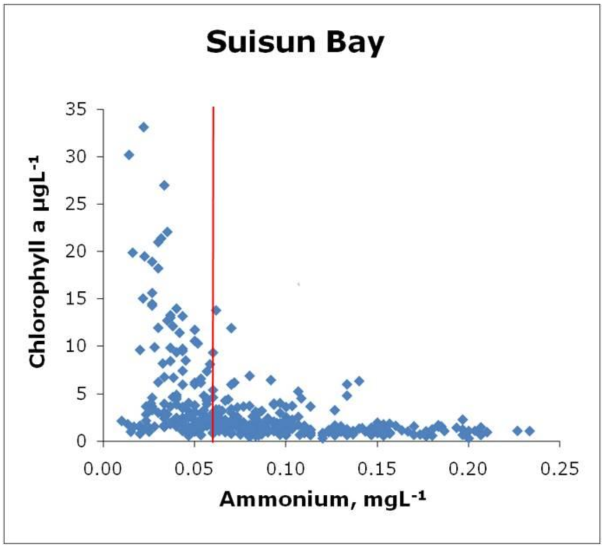

Figure 4. Chlorophyll-*a* concentration plotted with ammonium concentration in Suisun Bay. As NH_4 concentration increases above the level where inhibition is observed (red line at 0.056 mg L^{-1} NH_4), chl-*a* levels decline. (Source: Environmental Monitoring Program data)

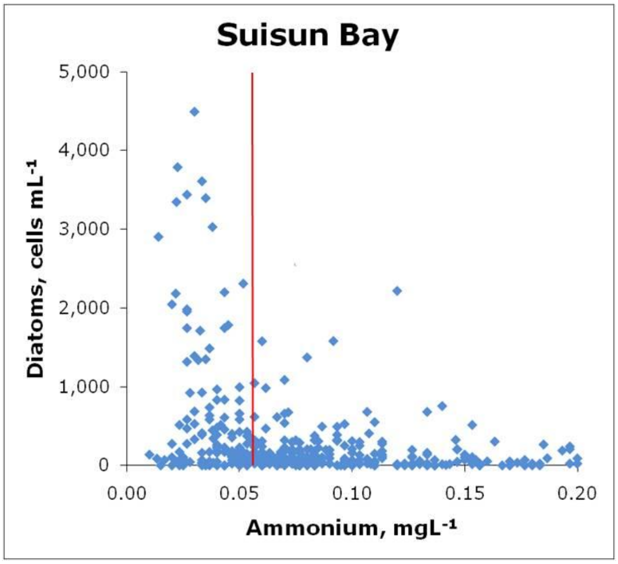

Figure 5. Diatom cell count plotted with ammonium concentration in Suisun Bay**.** As NH_4 concentration increases above the level where inhibition is observed (red line at 0.056 mg L^{-1} NH_4), diatom abundance declines. (Source: Environmental Monitoring Program data)

Similar threshold values have been reported by others. Lomas and Glibert (1999) described the threshold for inhibition of NO_3 uptake at NH_4 levels of approximately 1 µmol L^{-1} (0.014 mg L^{-1}). Yoshiyama and Sharp (2006) saw a "striking decline in production at NH_4 levels above a low threshold (around 10 µmol L^{-1})" (0.14 mg L^{-1}).

The Delta's algal species composition has shifted over the past decades from diatoms to smaller and lower quality food species such as flagellates, cryptophytes and cyanobacteria (Lehman, 2000*;* Lehman *et al*., 2005*;* Lehman et al., 2010; Jassby *et al*., 2002; Sommer *et al*., 2007*;* Glibert, 2010; Glibert et al., 2011; Winder and Jassby, 2010). Dugdale et al. (2012) developed a conceptual model that correctly predicted the development of two rare, spring phytoplankton blooms in Suisun Bay based on only three criteria: the rate of NH_4^+ loading (based on present day sewage effluent loads), the water column concentration of NH_4^+, and river flow (analogous in steady-state chemostat growth to "washout"). This conceptual model was further advanced in a one-dimensional, N-based model (Dugdale et al., 2013), having the unique features of the inclusion of terms for the time-varying rates of maximum NO_3^- uptake as a function of NO_3^- concentration and for inhibition of NO_3^- uptake by NH_4^+. The modeled high-biomass, NO_3^--based, high-productivity state is analogous to the pre-1982, diatom era of the Bay-Delta. The importance of NH_4 inhibition of NO_3 uptake was considered to be a necessary interaction to include in a recent model of the emergent phytoplankton community in the California Current System (Goebel et al. 2010).

The evidence is continuing to mount that the increasing loads of NH4 are an important contributor to the observed changes in phytoplankton community. The emerging experimental data – assembled from samples collected from the Bay-Delta and elsewhere- provide direct experimental evidence that dichotomous phytoplankton communities develop when enriched with the same absolute concentration of NO_3 and NH_4, even when sufficient N nutrient was available to the community prior to the N inoculations. Although there is much yet to be learned about the role of nutrient control in many aspects of the Bay-Delta ecosystem, the patterns of response by algal communities to NH_4 vs. NO_3 are consistent with observations in other systems and are consistent with the differential physiology of different algal groups.

Total Ammonia Toxicity

In addition to altering phytoplankton community structure, growth rates and abundance, ammonia is also toxic to some higher trophic level organisms. Scientists at University of California, Davis have investigated the effects of total ammonia nitrogen (NH_3 + NH_4) on the growth, reproduction and survival of the calanoid copepod *Pseudodiaptomus forbesi* using a full life-cycle bioassay approach (Teh et al. 2011). *P. forbesi* is an important prey item for the young of many fish species in the Bay-Delta including delta smelt and longfin smelt (Nobriga 2002; Hobbs et al. 2006; Feyrer et al. 2003). Teh et al. (2011) found that total NH_3+NH_4 at 0.36 mg L^{-1} (25.7 µmol L^{-1}) significantly affects the recruitment of new adult copepods, and that total NH_3+NH_4 at 0.38 mg L^{-1} (27.1 µmol L^{-1}) significantly affects the number of newborn nauplii surviving to 3 days (Teh et al. 2011). For comparison, monthly water samples collected between 2009-2010 from the Sacramento River between Hood and Isleton, approximately 30 miles downstream from the discharge point for the Sacramento Regional Wastewater Treatment Plant, exceeded the level of 0.36 mg/L NH_4-N 44% of the time (Figure 6).

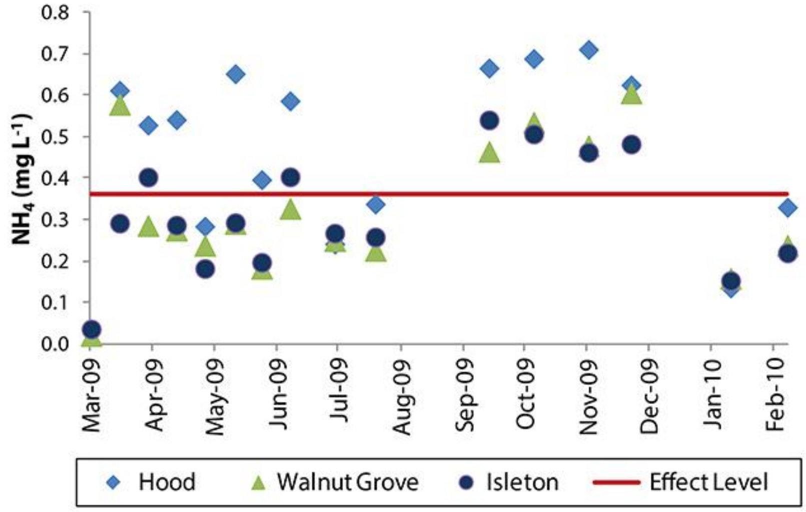

Figure 6. Ammonium concentrations in the Sacramento River measured at Hood, Walnut Grove, and Isleton between 2009 and 2010. Hood and Isleton are approximately 8 and 30 miles downstream of the discharge, respectively. The horizontal line at 0.36 mg L^{-1} is the level at which significant toxicity to copepods is observed. Data from Foe et al. (2010).

The Teh et al. (2011) study was recently cited in the U.S. Fish and Wildlife Service 12-month finding on the petition to list the Bay-Delta longfin smelt as threatened or endangered under the ESA. (77 Fed. Reg. 19755, 19776 [April 12, 2012].) The proposed rule states that "[a]quatic insects on which the longfin smelt relies upon for food have been shown to be sensitive to ammonia." (77 Fed. Reg. 19776.) The proposed rule states that "[a]mmonia also can be toxic to several species of copepods important to larval and juvenile fishes." (*Id.*) The toxic effect of total ammonia is a major stressor on aquatic life that has a pervasive impact across the Bay-Delta estuary.

Further, the U.S. Environmental Protection Agency's (USEPA) Bay-Delta Action Plan highlights concerns with aquatic life toxicity caused by total ammonia nitrogen and identifies total ammonia levels as one of the suspected contributors to the pelagic organism decline in the Bay-Delta (USEPA 2012). In the Bay-Delta Action Plan, USEPA states that they will finalize the new national ammonia aquatic life criteria and they encourage the Regional Boards to consider adopting the criteria and using the criteria to develop effluent limitations for ammonia. USEPA adopted the new aquatic life water quality criteria for ammonia in 2013, which are more stringent than previous criteria adopted in 1999 and consider ammonia toxicity to freshwater mussels (USEPA 2013).

Nitrogen:Phosphorus

Extensive research has found that the N:P ratio also has profound effects on community structure. The principles of ecological stoichiometry suggests that different organisms will dominate under different relative proportions of critical elements (C, N, or P) due to differences in allocation of C, N and P in the various structures that form the biomass of different types of organisms (Sterner and Elser, 2002). As noted by Hall (2009, p. 504), "Ecological stoichiometry formalizes what should be obvious: Organisms interacting in food webs are composed of different elements, such as C, N, or P. As a result, energy and nutrient flow through consumer-resource interactions obey fundamental constraints." Elemental differences in biomass are found at all levels of organismal structure across trophic levels, from the subcellular to the macrocellular structural components (Sterner and Elser, 2002). The Redfield ratio (Redfield, 1934, 1958), in which organismal C:N:P ratios are assumed to be in the proportion of 106:16:1 by atoms, is likely the most well-known stoichiometric relationship.

The N:P ratio of nutrients has doubled in the Bay-Delta estuary over the last 35 years as is apparent from the data on Figure 7. These increases are a result not only of the increasing total N load (due to increasing effluent as well as other sources), but also as a function of declining P loads (Van Niewenhuyse 2007; Glibert 2010, Glibert et al. 2011).

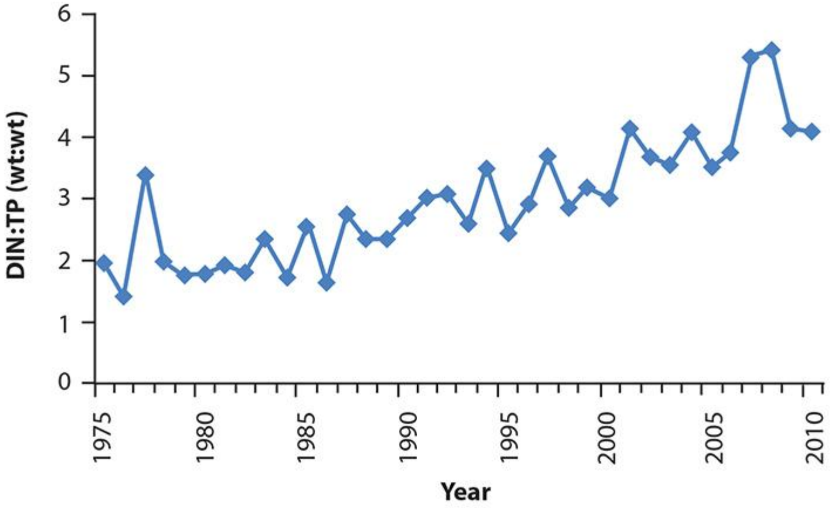

Figure 7. Average annual (March-November) ratio of dissolved inorganic nitrogen to total phosphorus has doubled in the Bay-Delta**.** (Source: IEP monitoring data from stations in Suisun Bay and the confluence (D4, D6, D7, D8)).

There are a number of strategies available to different types of phytoplankton for coping with an environment where nutrient ratios are not in proportion to their internal requirements (Glibert and Burkholder 2011). For example, cell size is an important determinant of elemental composition (Harris 1986; Finkel et al. 2010). Small cells have a lower requirement for P due to the smaller need for structural components in the cell (Finkel et al. 2010). In comparison to diatoms, very small cyanobacteria such as *Synechococcus* have a much larger cellular ratio of carbon to phosphorus (C:P), on average (Finkel et al. 2010). This explains why small cells, such as *Synechococcus*, have been found to thrive in waters that are comparatively P poor, as is the case in Florida Bay (Glibert et al. 2004).

These basic principles of algal response to changing N:P have relevance to San Francisco Bay-Delta phytoplankton communities. Jassby (2008) stated:

> *A decrease in percentage of diatom biovolume occurred during 1975–1989, caused by both a decrease in diatoms and an increase in green algae, cyanobacteria, and flagellate species biovolume (Kimmerer 2005; Lehman 1996), i.e., probably in the direction of declining nutritional value per unit biomass. In principle, the total nutritional value of a community could decrease even as its biomass increases. Moreover, changes in size, shape, and motility of species comprising the phytoplankton community could also affect their availability as food particles for crustacean zooplankton and other consumers*.

There is strong support in the scientific literature for the proposition that the N:P ratio influences phytoplankton community composition. For example, in the Seto Inland Sea of Japan, removal of phosphorus also led to a shift in phytoplankton community structure from “nonharmful diatoms to harmful raphidophytes…and then finally to harmful/toxic dinoflagellates” (Yamamoto 2002). In this case the reduction in phosphorus which increased N:P, led to a change in phytoplankton community composition and was suggested to be “the major cause of the reduction in fishery production” (Yamamoto 2002).

In a retrospective analysis of 30 years of data from the Bay-Delta estuary, Glibert et al. (2011) found that the variation in these nutrient concentrations and ratios is highly correlated to variations in the total amount and composition of phytoplankton. This analysis revealed relationships between biological parameters and nutrients and/or nutrient ratios using both the original data and data that were adjusted for autocorrelation. At the phytoplankton level, as described earlier, there has been a decline in total chl-a and a decline in total diatoms over the past several decades in proportion to the increase in total inorganic N to total P (Figure 8). The change in chl-a with N:P is apparent in different regions of the Bay-Delta; as N:P increases, chl-a declines (Figure 9).

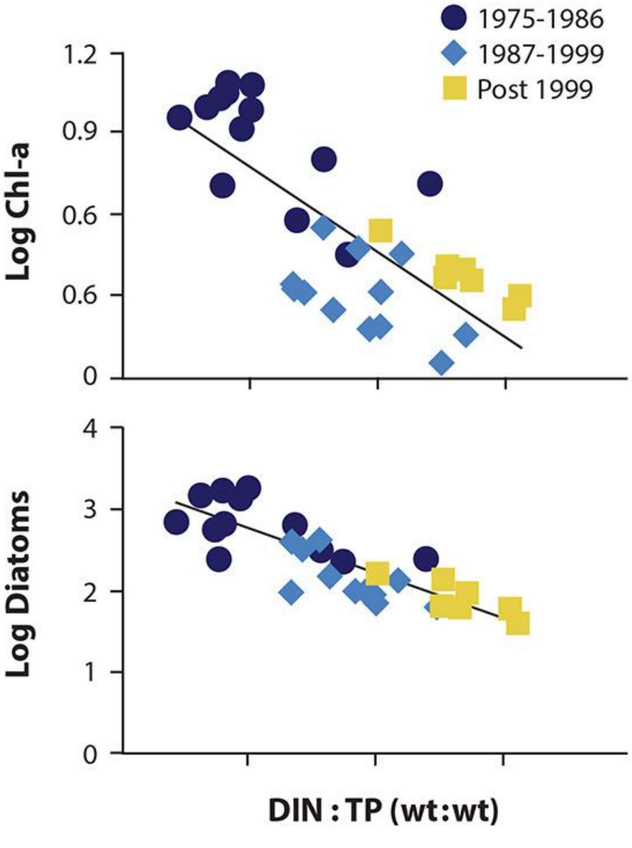

Figure 8. Change in the concentration of chl-*a* (µg L^{-1}) and abundance of diatoms (Bacillariophyceae, cells mL^{-1}) as a function of dissolved inorganic N to total phosphorus. A loss of total chl-*a* and a loss of total diatoms in the phytoplankton community have occurred over the past several decades in proportion to the change in total inorganic N to total P. The relationship is significant at $p<0.05$. Different periods of time are represented by different symbols: 1975-1986, filled circles; 1987-1999, diamonds; post-1999-filled squares. Data shown are for the years 1975-2005 and cover the region from the confluence to Suisun Bay. All data log-transformed. Data from Glibert et al. (2011).

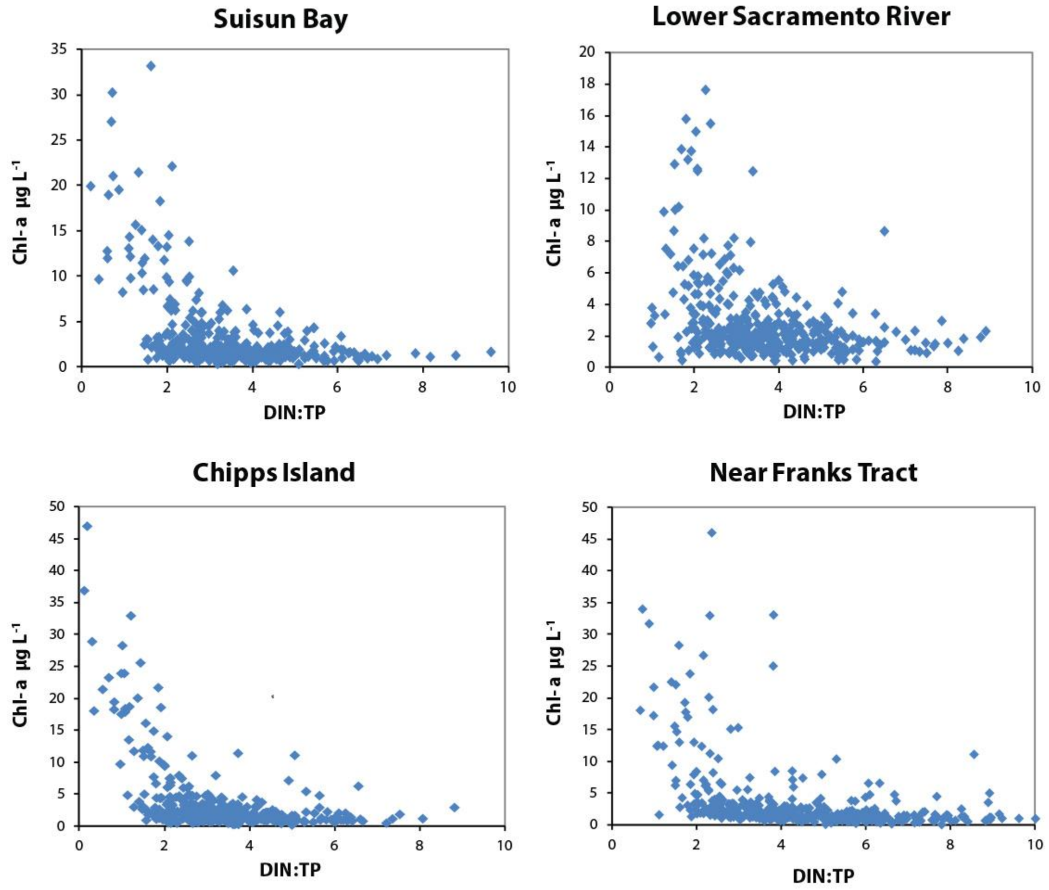

Figure 9. Chl-*a* concentration plotted against DIN:TP for subregions of the Delta, 1975-2011**.** As DIN:TP increases, there is a loss of chl-*a*. (Source: Environmental Monitoring Program data).

Fast-growing phytoplankton require proportionately more P to satisfy metabolic demands. Diatoms are typically fast-growing, and thus require proportionately more P to meet this metabolic demand. In ecological terms, they are considered a *r*-selected group, would be expected to have a low N:P biomass ratio (due to the high P cellular demand), and thus would be expected to be outcompeted if N:P in the environment increases. So-called *r*-selected species are out-competed when the environment changes (e.g., Heckey and Kilham 1988). In contrast, many cyanobacteria are considered to be *k*-selected, implying a slower growth rate and a higher metabolic N:P. In fact, "Reynolds (1984) singled out *Microcystis* as an example of a *k*-selected phytoplankter because it grows slowly in nature" (Heckey and Kilham 1988).

The balance of N:P can also affect other metabolic aspects of phytoplankton besides growth, including toxin production, cell membrane thickness, and other chemical constituents that have been considered to turn good food "bad" (Mitra and Flynn 2005). At the primary producer level, for example, emergent properties that can change in response to changes in elemental proportions include the relative proportions of ribosomes, enzyme activities, gene regulation, toxin production, cellular pigmentation complement, and ultimately the cell elemental composition, specifically, chl:carbon (Chl:C), C:N, and N:P (Glibert et al. 2013). Toxin production by numerous harmful algae has been shown to increase when the cells are grown under nutrient-imbalanced conditions and when there is a change in N or P availability (Flynn et al. 1994; Johansson and Granéli 1999; Granéli and Flynn 2006). In Daechung Reservoir, Korea, researchers found that toxicity of cyanobacteria was related not only to an increase in N in the water, but to the cellular N content as well (Oh et al. 2000). A recent report by Van de Waal et al. (2009) demonstrated in chemostat experiments that under high carbon dioxide and high N conditions, microcystin (an algal toxin) production was enhanced in *Microcystis*. Similar relationships were reported for a field survey of the Hirosawa-no-ike fish pond in Kyoto, Japan, where the strongest correlations with microcystin were high concentrations of NO_3 and NH_4 and the seasonal peaks in *Microcystis* blooms were associated with extremely high N:P ratios (Ha et al. 2009). Thus, not only is *Microcystis* abundance enhanced under high N:P, but its toxicity appears to be as well (Oh et al. 2000).

It is well accepted that the nutritional value of phytoplankton differs from one species to another. Toxin production can inhibit grazing. Some phytoplankton species are rejected by grazers due to their size. Others vary in their nutritional quality. For example, some diatom species produce certain highly unsaturated fatty acids that are essential for zooplankton reproduction (reviewed by Kilham et al. 1997) while flagellates generally produce different fatty acids than diatoms (Olsen 1999). Many trophic interactions, such as rates of growth or fecundity, are dependent on the acquisition of particular fatty acids, as a measure of the food quality of algae (e.g., Ahlgren et al. 1990; Coutteau and Sorgeloos 1997; Weers and Gulati 1997; Brett and Müller-Navarra 1997). In feeding experiments, Ger et al. (2010) observed reduced survival of the copepods, *Pseudodiaptomus* and *Eurytemora*, even when *Microcystis* was only a small portion of their available diet. Brett and Müller-Navarra (1997) developed a food quality rank for 10 species from 5 major phytoplankton groups based on the average of the observed change in the abundance of individual zooplankters that preyed upon these phytoplankton in growth bioassays. They and others (see Park et al. 2003) have applied a 0-1 scale of phytoplankton food quality in which cyanobacteria ranks at 0.2; green algae, 0.525; diatoms, 0.7; and cryptomonads, 0.95. Thus, a trend of decreasing diatoms and increasing cyanobacteria in the Bay-Delta would suggest, based on these rankings, a decrease in food quality for higher trophic levels.

Cloern and Dufford (2005) state, "[t]he efficiency of energy transfer from phytoplankton to consumers and ultimate production at upper trophic levels vary with algal species composition: diatom-dominated marine upwelling systems sustain 50 times more fish biomass per unit of phytoplankton biomass than cyanobacteria-dominated lakes."

For species that prey on phytoplankton (e.g., zooplankton), stoichiometry affects all aspects of behavior, such as growth rate, fecundity, and ultimately the success of different populations (Jeyasingh and Weider 2005, 2007), but may affect various life stages differently (Moe et al. 2005, p.31): "[a]n organism's requirements for different elements may vary throughout its life cycle, and thus certain life stages may be more sensitive than others to variation in the stoichiometry of its resource." For example, copepod juveniles have a relatively high demand for C, N, and P, but at a later stage, while C is still needed for metabolism, more P must be allocated to eggs. Therefore, P-poor food sources can disproportionately affect egg production while not affecting survival (Faerovig and Hessen 2003; Laspoumaderes et al. 2010). In a laboratory study where *Acartia tonsa* was fed diatoms grown on different N concentrations, Kiørboe (1989), confirmed that this zooplankter changes its feeding rate in response to phytoplankton of different chemical composition – thus, in response to food quality. Moreover, egg production followed the variation in algal N content and increased with increasing algal N. In the Bay-Delta, Slaughter and Kimmerer (2010) observed lower reproductive rates and lower growth rates of the copepod, *Acartia* sp. in the low salinity zone compared to taxa in other areas of the estuary. Their observation may be due to differences in nutrient stoichiometry between these areas.

In a review of field and laboratory-based research on stoichiometry in food webs, Hessen (1997) showed that a shift from copepods to *Daphnia* tracked N:P; copepods retain proportionately more N, while *Daphnia* are proportionately more P rich. Often, those organisms that are most able to retain the nutrient in limited supply, in this case P, have the competitive advantage in an unbalanced system. Glibert et al. (2011) illustrated a finding similar to Hessen's, that the decline in calanoid copepods in the Bay-Delta, and the invasion of cyclopoids tracked N:P over time. Variation in proportional densities of the calanoid copepod *Eurytemora* with the cyclopoid copepod *Limnoithona* over time has followed changes in the DIN:TP (dissolved inorganic nitrogen to total phosphorus) ratio (Figure 10), a pattern consistent with these grazers being responsive to changes in elemental stoichiometry and maintenance of altered dynamic equilibria on a long-term scale. In fact, Glibert et al. (2011) found relationships between many zooplankton species and nutrient composition. Results from whole-lake experimentation suggest that the N:P ratio is linked to alterations in zooplankton size, composition, and growth rate, as those animals with increased RNA allocation (more P available for growth) will grow at higher rates due to increased protein synthesis rates (Sterner and Elser 2002, Schindler 1974). Similar findings were reported from annual studies in the Baltic Sea (Walve and Larsson 1999).

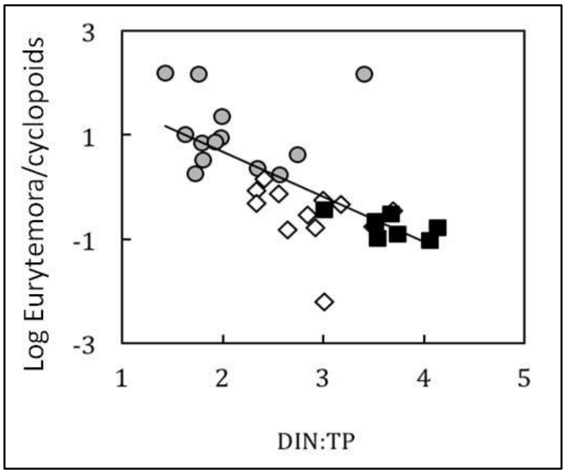

Figure 10. Change in the ratio of Eurytemora to cyclopoid copepods (all data log transformed) as a function of DIN:TP for annually averaged data from 1975-2005 for samples collected between the confluence and Suisun Bay**.** As DIN:TP increases, the proportion of Eurytemora to Cyclopoids decreases. Different periods of time are represented by different symbols: 1975-1986, filled circles; 1987-1999, diamonds; post-1999 filled squares. The correlation for these and for data that were detrended (not shown) are significant ($p<0.05$). From Glibert et al. 2011.

Superimposed on these empirical observations is consideration of whether substrate quality or food quality is altered on an episodic basis, or whether changes are long-term and sustained. As conceptualized by Hood and Sterner (2010), a change in predator growth rate depends on the extent to which a diet is sustained or switches between low-quality food and high-quality food as defined by the relative P content.

Higher Trophic Level Effects

Disproportionate N and P loads are now recognized to have effects at all scales, from genomic to ecosystems that need further empirical resolution (Peñuelas et al. 2012). When N:P availability changes, food webs change, biogeochemical cycling can change, and these changes can be positively reinforcing. Sterner and Elser (2002) state: "[s]toichiometry can either constrain trophic cascades by diminishing the chances of success of key species, or **be a critical aspect of spectacular trophic cascades with large shifts in primary producer species and major shifts in ecosystem nutrient cycling**" [emphasis added]. Just as different elemental ratios may affect the composition of the primary producers, different nutrient requirements of organisms occupying higher trophic levels will have an impact on their ability to thrive as community composition changes at the base of the food web. At the ecosystem scale, the total load and balance of nutrient elements have effects that propagate through the food web, with the potential of transforming ecosystems to new stable states. Although the shift in algal community composition in terms of diatoms and cyanobacteria has been emphasized above, this shift in the Bay-Delta estuary has been far more complicated. With the decline in water column chl-*a* and an increase in light availability, other primary producers have increased in abundance, including invasive macrophytes such as *Egeria densa* (Sommer et al. 2007; Nobriga et al. 2005; Glibert et al. 2011). *E. densa* may be particularly well suited to the low DIP:DIN environment of the Bay-Delta since it is able to access sediment bound phosphorus through its roots. In fact, similar increases in macrophytes were observed in many other systems in which N:P increased following N enrichment and P reduction, including the Potomac River, Chesapeake Bay, Ebro River in Spain, and the Rhine River in Germany (Glibert et al. 2011; Glibert 2012). Such macrophyte invasions can have profound impacts on ecosystems, not only because they alter the flow of C and the overall productivity of the system, but they also serve as "ecological engineers," decreasing nutrients through uptake, reducing turbidity by trapping sediments, and providing refuge for zooplankton and habitat for other species, including fish (Yarrow et al. 2009; Glibert 2012).

The interplay between nutrient stoichiometry and biogeochemistry is well illustrated when a system is driven to higher macrophyte productivity. Macrophytes can be highly productive, which can result in elevation of pH due to carbon drawdown in the process of photosynthesis. As noted by Glibert (2012), once pH is elevated, the fundamental physical–chemical relationships related to P adsorption–desorption in sediments change, as does N biogeochemistry (Jordan et al. 2008; Gao et al. 2012). Moreover, under increased pH conditions, the biogeochemistry of calcification is altered, increasing the potential for calcification and the growth of calcifying organisms. Thus, the change in the abundance of the clam *Potamocorbula amurensis* from the time of its introduction in the mid-1980s to 2005 has been shown to be highly and positively correlated to the increase in total N:total P ($r^2 = 0.46$; n = 20; $p < 0.01$; all data log transformed), and the average annual abundance of this species has also been found to be highly and positively correlated with mean annual average pH in the estuary ($r^2 = 0.64$; n = 19; $p < 0.01$; species abundance data log transformed) (Glibert et al. 2011). Interestingly, the Potomac River, Rhine River and the Ebro River have had similar invasions of macrophytes and *Corbicula* clams that relate to increases in N:P loading (Ibanez et al. 2008; Glibert et al. 2011; Glibert 2012).

In the Bay-Delta estuary, data show top-down grazing of phytoplankton by the clam *P. amurensis* exerts a strong control on phytoplankton biomass, as is also the case for other systems when invaded by bivalve mollusks. Prior interpretations, emphasizing stochastic invasions largely via ballast water exchange imply that the invasive event was the ultimate cause of the change in top-down control of phytoplankton. The ecological stoichiometric interpretation does not preclude strong top-down control of selected component organisms, nor ballast water exchange as the mechanism of introduction. The distinction is that, at the overall ecosystem level, the structuring of species is affected by alterations in nutrients and ecosystem biogeochemistry.

The arguments presented here make the case that bottom-up control contributed to the conditions that allowed *P. amurensis* to become a dominant regulator of phytoplankton production. In other words, invasive species effects and nutrient effects are interrelated. This interpretation is consistent with Ware and Thompson's (2005) insights from a broad survey of the relative contributions of "bottom-up" vs. "top-down" factors that potentially control fish catch in the coastal waters of the western U.S.; they, too, reported that bottom-up factors were more important.

Several recent reviews have investigated the stoichiometry of fish (Sterner and George 2000; Hendrixson et al. 2007; McIntyre and Flecker 2010). Not only does a strong shift in body N:P occur with growth stage (Pilati and Vanni 2007), but strong differences between taxonomic families also occur. In fact, Hendrixson et al. (2007) demonstrated, for 20 families of fish, that a phylogenic tree could be developed based on the body nutrient composition.

In the Bay-Delta estuary, numerous changes in fish community composition occurred in relation to phytoplankton and zooplankton changes, and to N:P (Glibert 2010; Glibert et al. 2011) (Figure 11).

Glibert et al. (2011) also found that total P “explained at least as much of the variability in delta smelt as did the [Feyrer et al. 2011] habitat index, and dinoflagellate abundance explained even more.” Unlike correlations with Bay-Delta outflow or with the location of the 2 practical salinity unit isohaline, where the underlying mechanisms driving the correlations are largely unknown, the nutrient relationships have a strong mechanistic explanation in ecological stoichiometry and stable state principles. For this reason, there is relatively low uncertainty that changes in nutrient stoichiometry in the Bay-Delta estuary, achieved through both external forces (altered land-based nutrient loads) and internal, organism-driven, assimilative and dissimilative processes, are related to community compositional changes (Glibert et al. 2011; Glibert 2012).

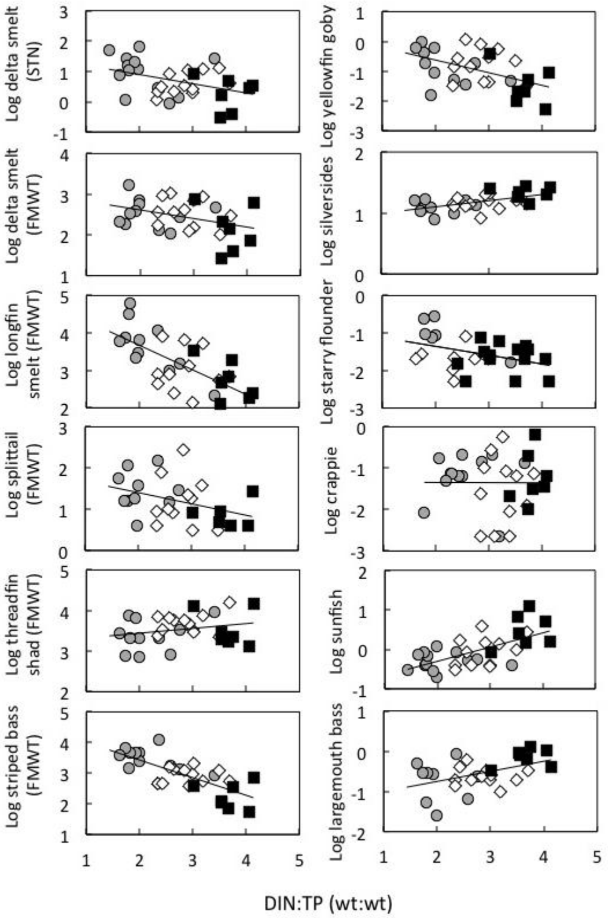

Figure 11. Changes in the abundance of major fishes in relation to ratio of dissolved inorganic nitrogen to total phosphorus from 1975-2005**.** Different periods of time are represented by different symbols: 1975-1986, filled circles; 1987-1999, diamonds; post-1999 filled squares. All data were log-transformed. The correlations for all fish except crappie were significant ($p<0.05$) in these data as well as in data that were detrended. Source: Glibert et al. (2011).

Total Nutrient Loads

Total nutrient load sets the upper limit on total primary production, and increases in nutrient loading are commonly associated with eutrophication. Nutrient levels in water diverted from the Delta are at concentrations that can produce nuisance algal and aquatic weed growth and adversely affect drinking water beneficial uses in downstream conveyance facilities and reservoirs. Algal and aquatic plant growth in the SWP conveyance facilities and downstream reservoirs is neither light limited nor inhibited by high ammonium concentrations since most of the ammonium from the Delta has been nitrified to nitrate. Elevated levels of nutrients (phosphorus and nitrogen compounds) stimulate nuisance algal and aquatic weed growth that includes production, by specific cyanobacteria, of noxious taste and odor compounds and algal toxins. In addition to algal produced taste and odor and algal toxin concerns, increases in algal and aquatic weed biomass can impede flow in conveyances, shorten filter run times and increase solids production at drinking water treatment plants, and add to organic carbon loading.

Frequently annual phosphorus concentrations at Clifton Court Forebay have averaged 0.11 mg/L and total nitrogen has averaged 0.87 mg L^{-1}. Phosphorus is significantly higher than the 0.020 to 0.042 mg L^{-1} that has been associated with a high risk of nuisance growth and eutrophication (USEPA 1980, 2001a). Levels of both nutrients exceed USEPA Ecoregion I phosphorus and total nitrogen reference conditions of 0.047 mg $L^{-1}$and 0.31 mg L^{-1}, respectively (USEPA 2001b)[1]. Ecoregion I includes the Central Valley.

Literature values and USEPA's ecoregion reference conditions[2] provide a starting point for determining whether nutrient concentrations in Delta waters are at levels that could cause water quality impairments, such as algal production of compounds that produce noxious tastes and odors. More importantly, there is already significant evidence of nutrient-related adverse impacts from Delta water. Through 2006, the Department of Water Resources (DWR) has applied algaecide treatments to Clifton Court Forebay for aquatic weeds and algae multiple times each summer. This practice was halted in 2007, however, over concerns of potential impacts to listed fish species. DWR has also treated the South Bay Aqueduct (SBA) to control algae that are stimulated by nutrient-rich Delta water. Including preventative treatments, DWR has treated the SBA for algal control between 10 and 16 times per year in recent years. Periodic treatment of the California Aqueduct and State Water Project (SWP) terminal reservoirs is also necessary for the same reason. Given the increasing environmental concerns about the use of copper-based algaecides, it is likely that effective control will become increasingly more difficult and reduce the ability of downstream users to manage algae-related problems in the future.

Eutrophication, ecological stoichiometry and alternate stable state theories combine to serve as a unifying framework for understanding the complexity of responses not only in the Bay-Delta estuary but also, more generally, in many comparative systems. This interpretation does not negate the importance of ecological invasions, habitat changes, multiple stressors and food-web complexities, but adds an explanatory mechanism to those interpretations through biogeochemistry and organismal stoichiometry. Ecological stoichiometry affects systems by setting elemental constraints on the growth of organisms. This, in turn, affects food quality and the relationships between predators and prey.

Examples of Responses to Nutrient Load Reductions

A growing body of literature documents improvements in ecosystem functions where nutrient loading is reduced and stoichiometric balance is restored. Reducing nutrient loading in the Chesapeake Bay, Tampa Bay, and coastal areas of Denmark has proven to be effective at reversing the harmful effects of previously undertreated discharges and restoring the native food webs. For example, within several years of increasing nutrient removal at the Blue Plains treatment plant in Washington D.C., N:P ratios in the Potomac River declined, the abundance of the invasive *Hydrilla verticillata* and *Corbicula fluminea* began to decline (Figure 12 showing *Corbicula Fluminea* and other relationships with N:P), and the abundance of native grasses increased (Ruhl and Rybicki 2010).

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[1] The reference condition is the 25th percentile of the nutrient data for sites within the ecoregion and is meant to represent the nutrient concentrations in minimally impacted water bodies.

[2] Significant questions have been raised about the use of reference conditions to establish regulatory criteria for nutrients. Nevertheless, they provide a starting point for evaluating water quality.

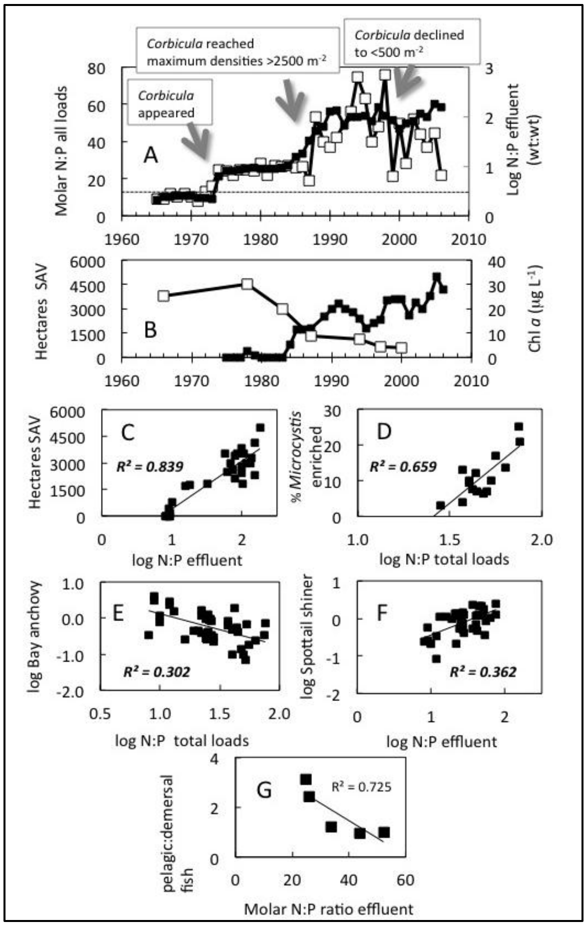

Figure 12. Comparative relationships for the Potomac River. Panel A shows the change in effluent N loading and the relative abundance of the invasive clam, *Corbicula fluminea*. *C. fluminea* appeared coincident with a sharp increase in N:P and increased in abundance as N:P increased. When N:P decreased sharply around 1999, *C. fluminea* abundance also declined sharply from >2500 m^{-2} to <500 m^{-2} Data derived from Dresler and Cory (1980), Jaworski et al. (2007), and Cummins et al. (2010). Figure reproduced from Glibert et al. (2011).

Tampa Bay provides another important example. Eutrophication problems in Tampa Bay were severe in the 1970s, with N loads approximating 24 tons per day, about half of which was due to point source effluent (Greening and Janicki 2006). Several years after nitrogen and phosphorus reductions were achieved, native seagrass began to increase. Lower nutrient discharges also had positive effects on the coastal waters around the island of Funen, Denmark (Rask et al. 1999). Since the mid 1980s, there has been a roughly 50% reduction in the loading of N and P in the region due to point source reductions. Again, native grasses returned and low oxygen problems were reversed.

Cloern (2001) provides additional examples of recovery following reductions in nutrient and waste inputs. Citing other researchers, Cloern (2001) shows improvements in dissolved oxygen levels in the Forth Estuary in Scotland following improvements in wastewater treatment. Citing a second study, Cloern (2001) shows increases in fish diversity in the Thames Estuary following improvements in wastewater treatment there (Figure 13).

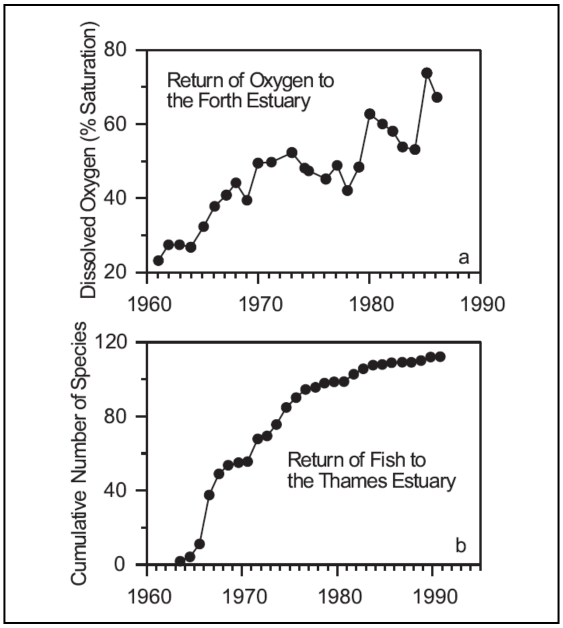

Figure 13. Two examples of recovery following actions to restore water quality in estuaries impacted by nutrient and waste inputs**:** (a) trend of increasing dissolved oxygen concentration (summer months) in the Forth Estuary, Scotland, following Improvements in wastewater treatment; (b) trend of increasing diversity of fishes in the Thames Estuary following implementation of advanced wastewater treatment and increases in oxygen concentrations (Source: Figure 20 from Cloern 2001).

Moreover, there is recent evidence that diatom blooms may be restored in the Bay-Delta estuary if NH_4 loading is reduced. In Suisun Bay, an unusual diatom bloom in Spring 2000 reached chl-*a* concentrations of 30 µg L^{-1} when NH_4 concentrations declined to 1.9 µmol L^{-1} (0.027 mg L^{-1}) (Wilkerson et al. 2006). Similarly, chl-*a* concentrations in Suisun Bay reached 35 µg L^{-1} during spring 2010 when NH_4 concentrations declined to 0.5 µmol L^{-1} (0.007 mg L^{-1}) (Dugdale et al. 2011, 2012). These blooms are comparable to spring chl-*a* levels from 1969 to 1977 (Ball and Arthur 1979) when NH_4 concentrations were 1.8 µmol L^{-1} (0.025 mg L^{-1}) during summer and 4.0 µmol L^{-1} (0.056 mg L^{-1}) during winter (Cloern and Cheng 1981).

In sum, ecological stoichiometry affects ecosystems by setting elemental constraints on the growth of organisms. However, as is the case with all conceptual frameworks, it must be viewed within the context of other factors in the environment, including the multiple stressors that now impact systems, as well as the scale (spatial, temporal and organismal) on which the system is being examined. Imbalances in stoichiometry may have impacts on ecosystems even at nutrient loads normally taken to be saturating or supersaturating. Ecological stoichiometry has several important implications for the health and sustainability of aquatic systems. Stoichiometric imbalances may accelerate transformations of nutrients or may alter the processes by which nutrients are cycled in the ecosystem, further altering nutrient availability or form for primary producers (Elser and Hamilton 2007, Nugraha et al. 2010). When food *quality* is linked to food web outcome, feedback effects and nutrient biogeochemical processes may play large roles in species success (Glibert 2012).

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Phytoplankton Blooms and Nitrogen Productivity in San Francisco Bay

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ABSTRACT: San Francisco Bay has been considered an HNLC or HNLG (high nutrient low chlorophyll or low growth) region with nonlimiting concentrations of inorganic nutrients yet low standing stocks of phytoplankton. Most of the studies leading to this conclusion come from the South Bay and little is known about nutrient processes and phytoplankton productivity in the northern and central parts of the estuary. Data collected over 3 yr (1999–2003) in Suisun, San Pablo, and Central Bays describe the availability of dissolved inorganic nitrogen (DIN), silicate, and phosphate and the seasonal variability in phytoplankton abundance. Rate measurements of fractionated nitrogen productivity provide the relative contributions of different forms of DIN (ammonium and nitrate) and different sized phytoplankton to the development of seasonal phytoplankton blooms. Regional differences in bloom dynamics are observed with Suisun Bay, the least saline, highest nutrient, most turbid region having less phytoplankton biomass and productivity than San Pablo and Central Bays, except in the abnormally wet spring of 2000. Spring blooms in San Francisco Bay are driven primarily by high rates of nitrate uptake by larger phytoplankton cells following a period of increased ammonium uptake that depletes the ambient ammonium. The smaller occasional fall blooms are apparently fueled mostly by ammonium uptake by small sized phytoplankton. The data suggest that the HNLC condition in the northern and central parts of San Francisco Bay is due primarily to light availability modulated by the interaction between ammonium and nitrate, and the relative amounts of the two forms of the DIN pool available to the phytoplankton.

Introduction

The San Francisco Bay (SFB) is of tectonic origin and can be separated into the northern estuary and the South Bay, which has been studied intensively (e.g., Conomos 1979; Nichols and Thompson 1985; Cloern 1996; Hollibaugh 1996; Kimmerer 2004). The northern estuary that has been less studied is dominated by the discharge at the Delta of the San Joaquin and Sacramento Rivers. Water passes through the embayments of the Suisun, San Pablo, and Central Bays with exit to the ocean through the Golden Gate (Peterson et al. 1996). Nutrient conditions in SFB have been considered nonlimiting with relatively high levels of nitrate (NO_3), silicate ($Si(OH)_4$), and phosphate (PO_4; Schemel and Hager 1986; Hager and Schemel 1996), resulting from primarily riverine and agricultural sources. Ammonium (NH_4) is also high in this urbanized estuary because of anthropogenic inputs (Hager and Schemel 1992). This upper region of SFB was ranked next to the lowest for phytoplankton production in a series of 24 river-dominated estuaries by Boynton et al. (1982).

Prior studies attribute a low standing stock of phytoplankton and low rates of primary productivity (Cole and Cloern 1984; Cloern 1996) to turbidity (Cloern 1987, 1991) resulting in light limitation (Alpine and Cloern 1988). Also implicated is benthic grazing (Nichols and Thompson 1985; Kimmerer and Orsi 1996; Lehman 2000) especially by invasive species such as the asian clam, *Potamocorbula amurensis* (Alpine and Cloern 1992), now known as *Corbula amurensis* (Coan 2002). Seasonal phytoplankton blooms have been observed following periods of high freshwater flow, when stratification reduces both the effects of benthic grazing and light limitation (Cloern 1982, 1984, 1991; Cloern et al. 1983; Lucas et al. 1998). Reported primary productivity values for the estuary (e.g., Cloern 2001) are mostly derived from the commonly used primary productivity model of Cole and Cloern (1984, 1987) recently updated for use in the Delta (Jassby et al. 2002) that empirically derives carbon fixation from values of chlorophyll, incident light, and transparency. Following the use of $Si(OH)_4$ depletion to estimate primary productivity in the northern estuary (Peterson et al. 1975, 1985), Kimmerer (2005) more recently used this approach to provide an integrated picture of primary production by diatoms. Direct measurements of primary productivity, nutrient assimilation, or phytoplankton growth rates in the northern estuary are rare compared to the South Bay (e.g., Cloern 1996, 2001; Jassby et al. 1996; Lucas et al. 1998). There are no published measurements of nitrogen productivity using the stable isotope ^{15}N, except for a year-long

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study (1998–1999) in Central Bay by Hogue (2000) and Hogue et al. (2005). Our study was carried out since there is little known about the variability of phytoplankton production and nutrient use in Suisun, San Pablo and Central Bays.

The aim of this study was to evaluate whether phytoplankton biomass and productivity were low in the northern estuary and to assess any environmental causes by measuring the seasonal variability of nutrients, size fractionated chlorophyll, and nitrogen assimilation. Data collected over 3 yr in Suisun, San Pablo, and Central Bays describe the relative contributions of different forms of dissolved inorganic nitrogen (DIN = NH_4 and NO_3) to the development of seasonal phytoplankton blooms and provides nitrogen productivity rate data for the region.

Materials and Methods

TIME SERIES SAMPLING

Surface water was sampled monthly from November 1999 to August 2003 aboard the R/V *Questuary* in San Francisco Bay at three locations described in Hogue et al. (2001) and on the United States Geological Survey (USGS) Water quality web site (http://sfbay.wr.usgs.gov/access/wqdata). These locations were in 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 (37°53.83′N, 122°25.5′W) and were sampled using 10-l Niskin bottles mounted on an SBE-33 carousel. During March and April sampling frequency was increased to weekly. Hydrographic data (temperature and salinity) were recorded from a Seabird SBE-19 CTD. A standard oceanographic Secchi disk was used to determine relative light penetration. Samples were taken for analyses of nutrients (NO_3, $Si(OH)_4$, PO_4, and NH_4), extracted chlorophyll *a* (chl *a*), and ^{15}N labeled NO_3 or NH_4 uptake. These analyses, including incubations for rate measurements, were carried out at the Romberg Tiburon Center near the Central Bay station location.

NUTRIENT, CHL *A*, AND ^{15}N UPTAKE ANALYSES

NO_3, $Si(OH)_4$, and PO_4 were analyzed using a Bran and Luebbe AutoAnalyzer II, NO_3 and PO_4 according to Whitledge et al. (1981), and $Si(OH)_4$ using Bran and Luebbe Method G-177-96 (Bran Luebbe AutoAnalyzer Applications 1999). If samples for NO_3, $Si(OH)_4$, and PO_4 analysis were frozen before analysis then they were thawed 24 h prior to analysis to avoid polymerization effects on $Si(OH)_4$ measurements and poor reproducibility (MacDonald et al. 1986). NH_4 was analyzed according to Solorzano (1969) after the samples were prefiltered through precombusted GF/F filters to remove sediment. Samples to be analyzed for NH_4 were never frozen. Chl *a* was determined by in vitro fluorometry (Arar and Collins 1992) using a Turner Designs Model 10 fluorometer, calibrated with commercially available chl *a* (Sigma Chemical Company or Turner Designs) on samples filtered onto either 25 mm Whatman GF/F filters (nominal pore size, 0.7 μm) or Nucleopore filters with either 5 or 10 μm pore size to collect the larger cells. ^{15}N uptake incubations were carried out in 280 ml polycarbonate bottles, for 24 h on incubation tables cooled with filtered SFB water and under window screening to expose them to 50% of ambient light. Because of steaming time from the sampling locations to the Romberg Tiburon Center where the incubations were carried out, most incubations were started towards the end of the light photoperiod. We selected a 24 h incubation period to encompass a natural light-dark photoperiod knowing that some regeneration of nutrients would result in an underestimation of uptake rates. On the assumption that any regeneration of organic nitrogen to NH_4 would occur at about the same rates as NH_4 uptake, the calculated underestimate of NH_4 uptake due to this regeneration would be 10–20%. ^{15}N inoculations were of trace additions (approximately 10% of ambient NO_3 or NH_4 concentrations) of either $K^{15}NO_3$ or $^{15}NH_4Cl$ (99 atom % ^{15}N). Incubations were ended by filtration onto precombusted (450°C for 4 h) 25 mm GF/F filters or Poretics silver filters with 5 μm pore size, and frozen until analysis for ^{15}N enrichment with a Europa Tracermass or PDZ 20/20 mass spectrometer system (Wilkerson and Dugdale 1992). Both transport rates (ρ) and biomass specific uptake (V; normalized to particulate nitrogen of the sample obtained by mass spectrometry) were calculated according to Dugdale and Wilkerson (1986). These data of ρNO_3 and ρNH_4 uptake are referred to as nitrogen productivity when they are summed, recognizing that there may be other small sources of nitrogen not measured here. Urea can be the predominant source of nitrogen fueling phytoplankton production in estuaries (Lomas et al. 2002; Glibert et al. 2005). Although urea was not measured in this study, there are a few spring and summer data available (Cochlan and Herndon unpublished data; Hogue unpublished data). Values measured in spring 2006 in San Pablo and Central Bays averaged 0.7 ± 0.2 μM (approximately 16% of the corresponding mean NH_4 concentrations) (Hogue unpublished data). Surface urea concentrations measured by Cochlan and Herndon (unpublished data) in SFB over the period of May to the end of August 2005 ranged from 0.3 to 3.8 μM (mean = 1.0 μM) on the eastern side of the Tiburon Peninsula (adjacent to Paradise Cay), whereas on the western side of the Peninsula (Richardson's Bay) they were 0.2 to 2.5 μM (mean also = 1.0 μM). These ambient urea concentrations represent on average 41% and 31% of the corresponding NH_4 concentrations for the eastern and western embayments, respectively, and only occasionally were urea levels equal or greater than NH_4 (Cochan and Herndon unpublished data). These values indicate that urea is unlikely to be a predominant source of nitrogen compared to NO_3 that can reach 35 μM (Hogue et al. 2005).

Results

TIME SERIES DATA FOR SUISUN BAY

Seasonal changes in temperature (Table 1) occurred with warmer summer temperatures (mean of 20°C for June–August) and cooling down to mean temperature of 10.96°C during the winter (December–February). Salinity values also varied seasonally (Fig. 1, Table 1) with fresher water (2 psu or below) typically in March and April. Maximum salinity values in Suisun were 13.40 psu, with values above 10 psu rare, occurring usually in December, except for August to October 2002. Inorganic nutrient concentrations were high throughout the year in Suisun Bay with $NO_3 > 30$ μM, $Si(OH)_4 > 200$ μM, and $PO_4 > 2$ μM (Fig. 1). The most variable nutrient was NH_4, ranging from 1.3 to almost 16 μM and showing seasonal maxima in December–January (accompanying the higher salinity water) and dips in April/May (2000, 2003, accompanying chlorophyll peaks) and September (2000 and 2001).

Chlorophyll concentrations in Suisun Bay (Fig. 1) were constant and low during the monthly sampling (1–2 μg l^{-1}) except for two peaks (blooms of 30 μg l^{-1} in April 2000 and 8.5 μg l^{-1} in April 2003). The chlorophyll during these peaks was dominated by cells >5 μm in diameter measured as fractionated chlorophyll data (Table 1).

NO_3 and NH_4 uptake rates (Fig. 1) by phytoplankton in Suisun Bay were low most of the year, both as the absolute rates (ρ) and the biomass specific rates (V that gives a more physiological estimate of the phytoplankters capacity; Table 2). There was an obvious peak in NO_3 uptake (ρ = 0.3 μmol l^{-1} h^{-1}; Fig. 1), accompanying the spring bloom condition on April 11, 2000. This maximum in ρNO_3 uptake rate was higher than any measured ρNH_4 uptake rate. The fractionated NO_3 uptake data show uptake in spring was dominated by cells >5 μm in size (Table 2). Interestingly the small increase in chlorophyll in May 2003 was not accompanied by higher NO_3 uptake in Suisun Bay, but instead showed a slight increase in NH_4 uptake.

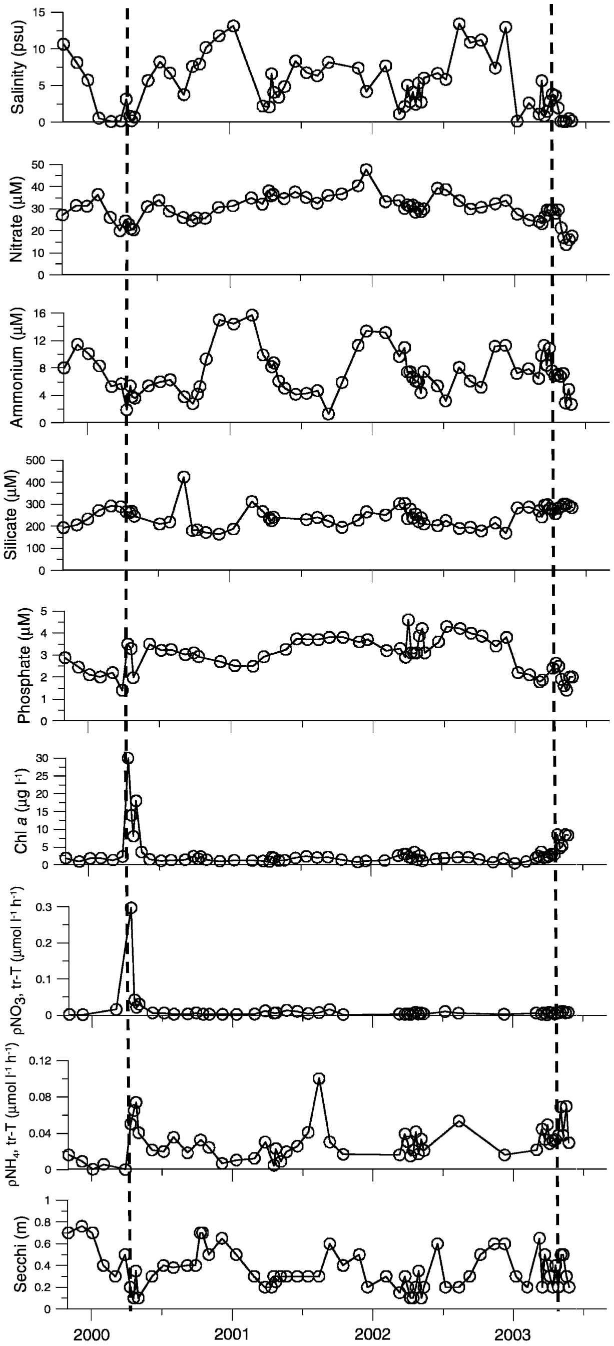

Fig. 1. Time series surface data from Suisun Bay from November 1999 to August 2003. Salinity (psu), NO_3 (μM), NH_4 (μM), $Si(OH)_4$ (μM), PO_4 (μM), chlorophyll *a* (μg l^{-1}), $\rho^{15}NO_3$ (μmol l^{-1} h^{-1}), $\rho^{15}NH_4$ (μmol l^{-1} h^{-1}), and Secchi depth (m). Dotted vertical lines show spring blooms described in text.

NH_4 uptake rates were more variable than NO_3 ranging from 0.0002 to 0.0247 μmol l^{-1} h^{-1} (Fig. 1), with peaks in April 2000 (ρ = 0.07 μmol l^{-1} h^{-1}), August 2001 (ρ = 0.1 μmol l^{-1} h^{-1}), and April and

TABLE 1. Mean surface hydrographic and chlorophyll data (±SD) and number of samples for Suisun, San Pablo, and Central Bays calculated as seasonal means for winter (December, January, February), spring (March, April, May), summer (June, July, August), and fall (September, October, November) from November 1999 to August 2003.

Bay	Season	Temperature (°C)	Salinity (psu)	NO_3 (μM)	$Si(OH)_4$ (μM)	PO_4 (μM)	NH_4 (μM)	Chl *a* (μg l^{-1})	>5 μm Chl (μg l^{-1})	% Chl > 5 μm	Secchi (m)
Suisun	Winter	10.96 (2.25) 11	7.04 (4.77) 11	32.5 (5.8) 12	235.0 (50.1) 12	2.6 (0.6) 12	11.3 (3.0) 12	1.2 (0.5) 12	0.8 (0.3) 12	66.7	0.5 (0.2) 12
	Spring	15.35 (1.95) 35	2.46 (1.94) 35	27.5 (6.02) 31	264.6 (26.5) 30	2.7 (0.8) 24	6.8 (2.4) 33	4.6 (5.8) 35	2.9 (3.5) 34	63.0	0.3 (0.1) 33
	Summer	20.21 (1.19) 9	7.54 (2.39) 9	34.4 (3.5) 9	216.7 (17.1) 7	3.6 (0.4) 9	5.3 (1.4) 9	1.8 (0.4) 9	1.3 (0.5) 9	72.2	0.3 (0.1) 9
	Fall	17.66 (6.04) 9	8.26 (3.39) 9	30.7 (5.5) 10	219.2 (74.5) 10	3.5 (0.4) 9	6.0 (3.3) 11	1.6 (0.6) 11	0.6 (0.3) 9	37.5	0.5 (0.1) 11
San Pablo	Winter	10.96 (0.85) 11	20.77 (5.63) 11	26.8 (5.9) 12	127.1 (45.9) 12	3.8 (4.2) 12	8.0 (2.6) 12	2.3 (0.9) 12	1.1 (0.6) 12	47.8	0.9 (0.2) 12
	Spring	14.76 (1.40) 34	17.08 (5.19) 34	18.1 (4.2) 30	128.0 (41.2) 31	3.4 (4.9) 25	3.5 (1.9) 34	6.5 (3.6) 36	5.2 (4.0) 36	80.0	0.7 (0.4) 33
	Summer	19.06 (1.00) 9	23.32 (1.50) 9	23.9 (5.9) 9	106.2 (17.5) 9	3.6 (0.7) 9	4.1 (2.2) 9	3.0 (1.6) 9	1.7 (0.7) 9	56.7	0.7 (0.4) 9
	Fall	17.13 (1.89) 13	24.28 (5.17) 13	19.0 (3.8) 14	96.3 (6.57) 14	3.1 (0.3) 14	5.4 (2.2) 14	3.2 (1.2) 14	1.2 (0.7) 14	37.5	1.2 (0.5) 14
Central	Winter	11.48 (0.74) 12	27.29 (3.48) 12	21.7 (4.44) 11	75.9 (29.3) 12	2.4 (0.4) 11	6.7 (2.2) 12	2.1 (0.7) 12	1.0 (0.4) 12	47.6	1.1 (0.3) 11
	Spring	13.68 (0.91) 36	25.04 (3.80) 36	15.6 (3.7) 31	80.6 (26.9) 31	2.1 (0.7) 25	3.2 (1.7) 34	5.8 (2.8) 35	4.2 (3.8) 28	72.4	1.1 (0.4) 36
	Summer	17.14 (1.16) 10	28.33 (1.57) 10	20.7 (3.6) 9	73.0 (19.7) 9	2.9 (0.6) 9	4.9 (1.7) 9	3.4 (1.5) 9	0.9 (0.4) 8	26.5	1.1 (0.4) 10
	Fall	16.01 (1.34) 13	30.40 (1.09) 13	14.0 (3.6) 13	57.4 (10.9) 13	2.5 (0.4) 13	6.1 (1.3) 14	4.0 (1.8) 14	1.5 (0.8) 11	37.5	1.6 (0.3) 14

TABLE 2. Mean surface nitrogen uptake and primary productivity values (±SD) and number of samples for Suisun, San Pablo, and Central Bays calculated as seasonal means for winter (December, January, February), spring (March, April, May), summer (June, July, August), and fall (September, October, November) from November 1999 to August 2003.

Bay	Season	VNO_3 in all cells ($\times 10^{-3}$ h^{-1})	ρNO_3 in all cells ($\times 10^{-3}$ $\mu mol\ l^{-1}\ h^{-1}$)	ρNO_3 in cells >5 µm ($\times 10^{-3}$ $\mu mol\ l^{-1}\ h^{-1}$)	VNH_4 in all cells ($\times 10^{-3}$ h^{-1})	ρNH_4 in all cells ($\times 10^{-3}$ $\mu mol\ l^{-1}\ h^{-1}$)	ρNH_4 in cells >5 µm ($\times 10^{-3}$ $\mu mol\ l^{-1}\ h^{-1}$)	Calculated ρC (µg l^{-1} d^{-1})	f ratio
Suisun	Winter	0.27 (0.83) 8	2.04 (1.59) 8	0.61 (0.51) 8	3.04 (1.75) 8	11.13 (8.17) 8	4.65 (5.19) 8	25.02	0.15
	Spring	2.53 (7.60) 32	17.69 (1.82) 32	10.52 (31.2) 31	3.74 (2.59) 33	32.23 (18.9) 33	27.79 (28.7) 31	94.9	0.35
	Summer	0.69 (1.50) 9	7.06 (4.9) 9	3.65 (5.0) 9	6.09 (6.6) 9	37.3 (35.9) 9	16.35 (16.78) 9	84.3	0.16
	Fall	0.030 (2.2) 10	4.68 (5.24) 70	2.2 (3.17) 7	2.98 (5.24) 7	24.55 (0.61) 7	17.79 (5.9) 5	55.6	0.16
San Pablo	Winter	0.6 (0.3) 7	2.33 (1.37) 7	0.5 (0.42) 7	6.11 (4.21) 7	20.45 (13.4) 7	10.81 (8.90) 7	43.3	0.10
	Spring	6.76 (11.89) 33	49.4 (70.69) 33	43.05 (63.0) 32	8.84 (5.35) 35	75.63 (35.94) 35	61.1 (86.7) 32	233.4	0.40
	Summer	3.2 (6.49) 9	8.24 (8.89) 9	5.7 (6.69) 9	7.52 (6.95) 9	30.50 (31.96) 9	20.67 (23.44) 9	73.6	0.21
	Fall	1.85 (3.57) 13	13.10 (25.4) 13	9.61 (15.6) 13	15.23 (15.1) 9	52.01 (43.19) 9	37.58 (37.31) 9	123.8	0.20
Central	Winter	0.79 (0.43) 7	2.88 (1.42) 7	1.55 (1.71) 7	5.98 (2.25) 7	19.37 (7.78) 7	16.48 (15.77) 7	42.3	0.13
	Spring	6.44 (7.49) 30	59.33 (82.5) 30	57.91 (87.82) 29	8.56 (5.01) 32	67.76 (140.22) 32	47.11 (33.26) 29	241.6	0.47
	Summer	3.0 (1.97) 89	11.53 (7.45) 8	8.24 (8.22) 9	10.1 (7.05) 9	38.46 (38.75) 9	32.0 (33.32) 9	95.0	0.23
	Fall	1.56 (1.36) 12	10.63 (12.07) 12	8.23 (10.47) 13	12.11 (8.78) 9	70.1 (173.4) 9	44.0 (38.93) 9	153.5	0.13

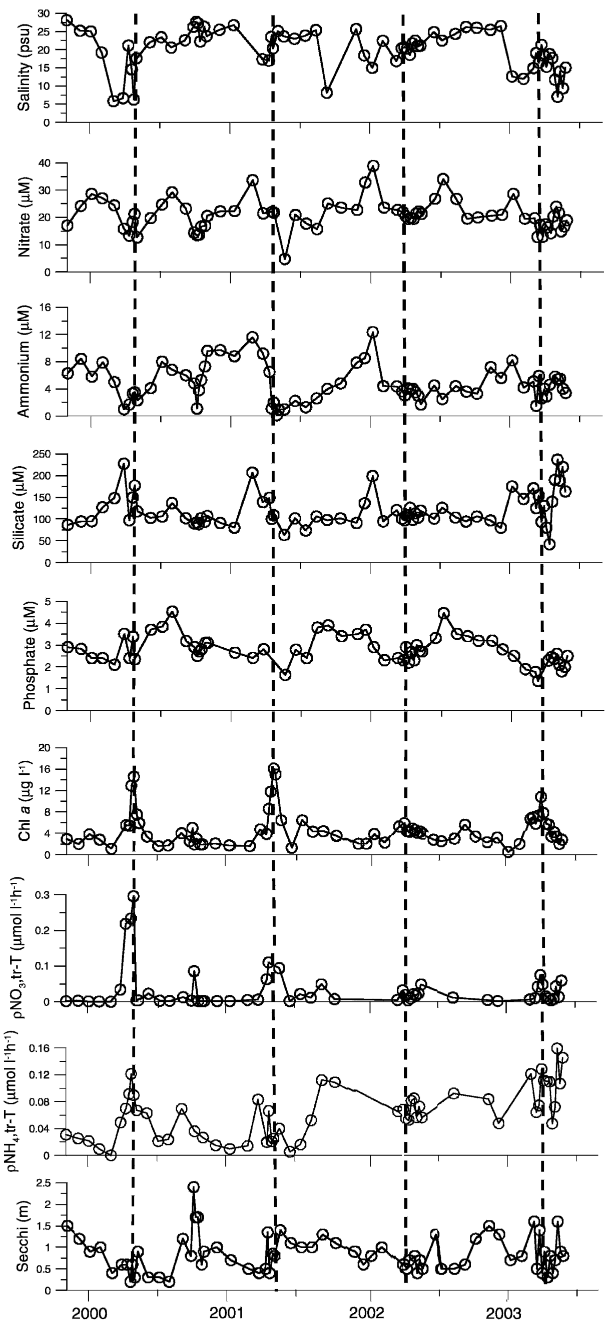

Fig. 2. Time series surface data from San Pablo Bay from November 1999 to August 2003. Salinity (psu), NO_3 (µM), NH_4 (µM), $Si(OH)_4$ (µM), PO_4 (µM), chlorophyll *a* (µg l^{-1}), $\rho^{15}NO_3$ (µmol l^{-1} h^{-1}), $\rho^{15}NH_4$ (µmol l^{-1} h^{-1}), and Secchi depth (m). Dotted vertical lines show spring blooms described in text.

September 2002 and May 2003, accompanied by slightly higher chlorophyll values.

Light availability was low most of the year with maximal light penetration (Secchi depths of 0.6 to 0.8 m) occurring from November to December and with the lowest values of 0.1 to 0.2 during April–May of each year (Fig. 1).

Time Series Data for San Pablo Bay

A similar range of mean seasonal temperatures to that in Suisun Bay was measured in San Pablo Bay with higher values in summer (mean of 19.06°C) and lower values in winter (mean of 10.96°C, Table 1). Salinity values (Fig. 2) were different than Suisun Bay with higher minimum values (>6 psu) and maxima reaching almost 28 psu. Lower values (i.e., <10 psu) occurred in March 2000, May and September 2001, and May 2003.

Nutrient concentrations showed greater variability than in Suisun Bay, with NO_3 (4.8–38.9 µM), $Si(OH)_4$ (41.8–236.6 µM), and PO_4 (1.36–4.53 µM; Fig. 2) showing peaks in January, February, and March of all years and small peaks in August 2000, September 2001, and July 2002. NH_4 concentrations were less than in Suisun Bay, but like Suisun, maximal concentrations (12 µM) occurred during the winter (December, January, February) months. The maximal value in January 2003 only reached 8 µM compared to 12 µM in Suisun Bay. Chlorophyll concentrations tended to be higher than in Suisun, and showed spring increases from the annual mean concentration of 3.5 µg l^{-1} (not shown). The spring peaks occurred later than in Suisun, reaching 15 µg l^{-1} in May 2000, 16 µg l^{-1} in May 2001, 6 µg l^{-1} in late March 2002, and 11 µg l^{-1} in April 2003, at the same time as the lowest NH_4 concentrations were measured. The spring concentrations of chlorophyll were dominated by the larger phytoplankton cells (Table 1).

Nitrogen transport rates tended to be higher in San Pablo Bay than Suisun Bay. Increases in NO_3 uptake were observed every spring (Fig. 2) and also small increases in fall 2000 and 2001, at the same time as the increases in chlorophyll concentrations. The April 2002 bloom had lower chlorophyll and lower NO_3 uptake rates than the other years in San Pablo Bay. The fractionated uptake rates show the NO_3 uptake during spring times to be dominated by larger cells (Table 2). During the times with increased chlorophyll, NH_4 uptake (Fig. 2) did not reach the highest values measured for NO_3 uptake (maximum $\rho NO_3 = 0.3$ µmol l^{-1} h^{-1} versus maximum $\rho NH_4 = 0.16$ µmol l^{-1} h^{-1}). Both sources of DIN are used but in the spring NO_3 uptake exceeds NH_4 (i.e., $\rho NO_3 > \rho NH_4$) and is the major source used for growth.

Light penetration and availability was greater in San Pablo (Fig. 2) than Suisun with average Secchi depth of 0.9 m, with minima of 0.2 m in April and clearer waters in November (maximum of 2.4 m).

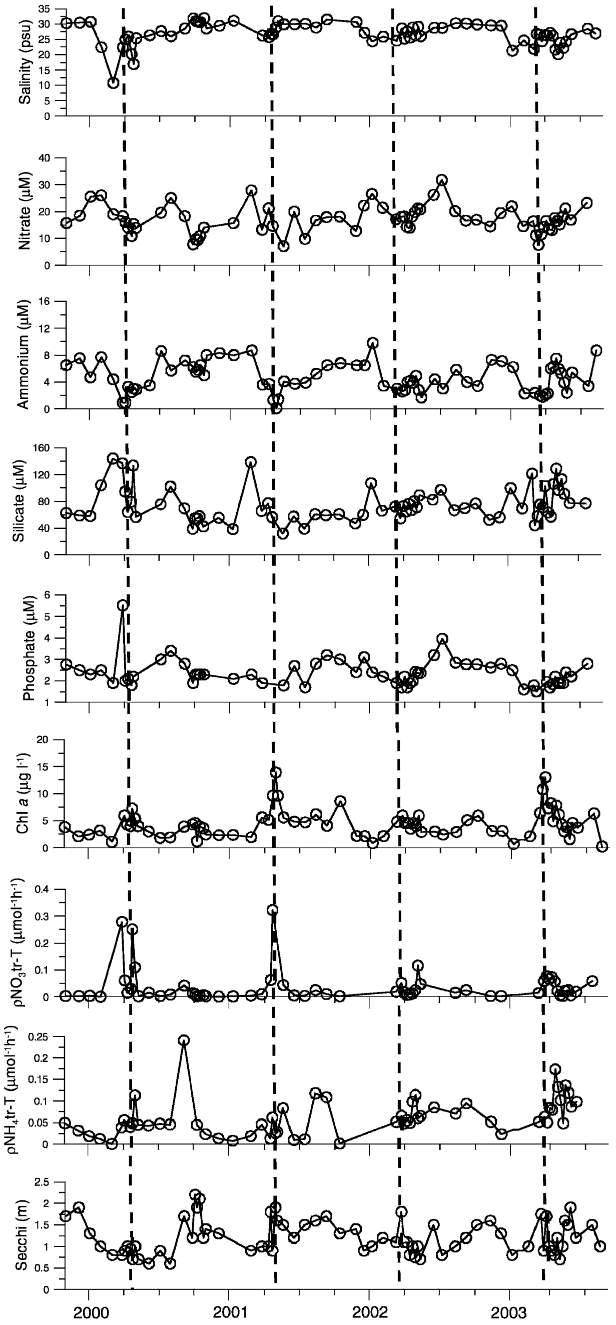

Fig. 3. Time series surface data from Central Bay from November 1999 to August 2003. Salinity (psu), NO$_3$ (μM), NH$_4$ (μM), Si(OH)$_4$ (μM), PO$_4$ (μM), chlorophyll *a* (μg l^{-1}), ρ^{15}NO$_3$ (μmol l^{-1} h^{-1}), ρ^{15}NH$_4$ (μmol l^{-1} h^{-1}), and Secchi depth (m). Dotted vertical lines show spring blooms described in text.

Time Series Data in Central Bay

Surface temperatures in Central Bay showed the same seasonal trends as the other bays but with lower mean summer temperatures (17.14°C versus 19.06°C in San Pablo and 20.21°C in Suisun Bays; Table 1). Salinities were much more oceanic, saltier, and less variable (Fig. 3) than the other bays with most values >25 psu (compared to 6 psu in San Pablo and 2 psu in Suisun), except in March 2001 when there was a large freshwater input (10.8 psu). Maximal values of 32 psu were measured, typically in September.

Nutrients tended to be lower in Central Bay (maximum NO$_3$ = 31.7 μM, NH$_4$ = 9.8 μM, Si(OH)$_4$ = 144 μM, and PO$_4$ = 5.5 μM; Fig. 3) than Suisun and San Pablo Bays. NH$_4$ was almost depleted in March 2000, similar to San Pablo Bay, and also in March–April 2001, 2002, and 2003. Seasonal maxima in nutrients were shifted slightly earlier than San Pablo with peaks in January and February each year and also in July 2000, June 2002, and June 2003. As in San Pablo Bay, nutrient decreases followed the peaks and were matched by increases in chlorophyll later.

Seasonal spring increases in chlorophyll (Fig. 3) matched those of San Pablo with maxima (above the average 3.5–4 μg l^{-1}) in April–May 2000 and 2001 of 7 and 14 μg l^{-1} and April 2002 and March 2003 of 6 and 13 μg l^{-1}. There were also small increases in October 2000, 2001, and 2002. The fractionated chlorophyll data showed that biomass was dominated by the larger cells in spring (Table 1).

NO$_3$ uptake (ρNO$_3$) in Central Bay (Fig. 3) peaked each spring accompanying the chlorophyll blooms, reaching 0.25 μmol l^{-1} h^{-1} in April 2000, 0.32 μmol l^{-1} h^{-1} in April 2001, 0.1 μmol l^{-1} h^{-1} in May 2002, and 0.09 μmol l^{-1} h^{-1} in March 2003. Specific uptake rates (VNO$_3$) showed the same seasonal trend (Table 2). Larger phytoplankton contributed significantly at times when there was higher mean ρNO$_3$ uptake. Unlike in Suisun and San Pablo Bays, ρNH$_4$ uptake did not show the same springtime variability as ρNO$_3$ uptake. NH$_4$ uptake (Fig. 3) never reached the maximal values of ρNO$_3$ uptake (maximum ρNH$_4$ = 0.24 μmol l^{-1} h^{-1}) and showed peaks in September 2000, 2001, and 2002 as well as in spring.

The trend for deeper Secchi depths going seaward continued and the annual mean Secchi depth in Central Bay was 1.2 m (not shown) with a maximum of 2.2 m. Shallowest values (0.6 m) were measured in April (Fig. 3), as was observed in San Pablo and Suisun Bays although the very shallow Secchi depth of 0.1 m measured in Suisun was not observed in Central Bay.

Mean Seasonal Data for the Three Bays

To be able to compare the three bays more easily, the 3 yr surface data were condensed to mean seasonal values (Tables 1 and 2), using data from three monthly cruises for each season of the 3 yr except in spring when the sampling frequency was increased to weekly and means are based upon more cruises. Typically, winter (December–February), summer (June–August), and fall (September–November) means are based on 10 ± 1 samples and spring (March–May) means on 30 ± 5 samples. The winter values provide a way to assess the effect of freshwater and ocean inputs of nutrients to the three bays, since biological activity is minimal. Mixing diagrams (of winter mean nutrient concentrations versus salinity, Fig. 4), with straight lines linking the three bays indicate that the sources of all three high nutrient concentrations (NO_3, $Si(OH)_4$, and NH_4) are fresher waters, from the head of the estuary, diluted to lower values in the lower two bays (San Pablo and Central Bays) by the low nutrient, high salinity ocean water. PO_4 (not shown) exhibited no such clear pattern with maximum values in San Pablo Bay suggesting a strong local source of that nutrient.

When mean nutrient values for all four seasons are plotted together against salinity, the seasonal progressions from winter to fall of $Si(OH)_4$, NO_3, and NH_4 in the three bays can be observed (Fig. 5). For each nutrient, the location of each bay between the freshwater and oceanic end points is clearly indicated without overlap. The seasonal cycle for $Si(OH)_4$ commences with an increase from winter to spring, most noticeably in Suisun Bay due to increased freshwater input followed by a decrease to summer and fall as salinity increases (runoff and freshwater input decreases). NO_3 decreases from winter to spring due to uptake of NO_3 by the phytoplankton (Fig. 6, Table 2) as salinity decreases; then increases in summer and decreases again in fall (Fig. 5). $Si(OH)_4$ does not track the NO_3 decreases from winter to spring as $Si(OH)_4$ is also taken up biologically but the amount is overwhelmed by the very high concentrations of $Si(OH)_4$ in the freshwater input. As runoff decreases into summer, $Si(OH)_4$ concentrations decrease (as the high $Si(OH)_4$ supply in the freshwater input ceases) but mean NO_3 concentration does not since the spring biological uptake of NO_3 has stopped and NO_3 remains in the water. The fall decreases in both $Si(OH)_4$ and NO_3 are correlated with salinity increases and are mostly due to dilution by low nutrient, salty oceanic water. NH_4 concentration declines rapidly from winter to spring (Fig. 5), partly due to dilution by fresh water and

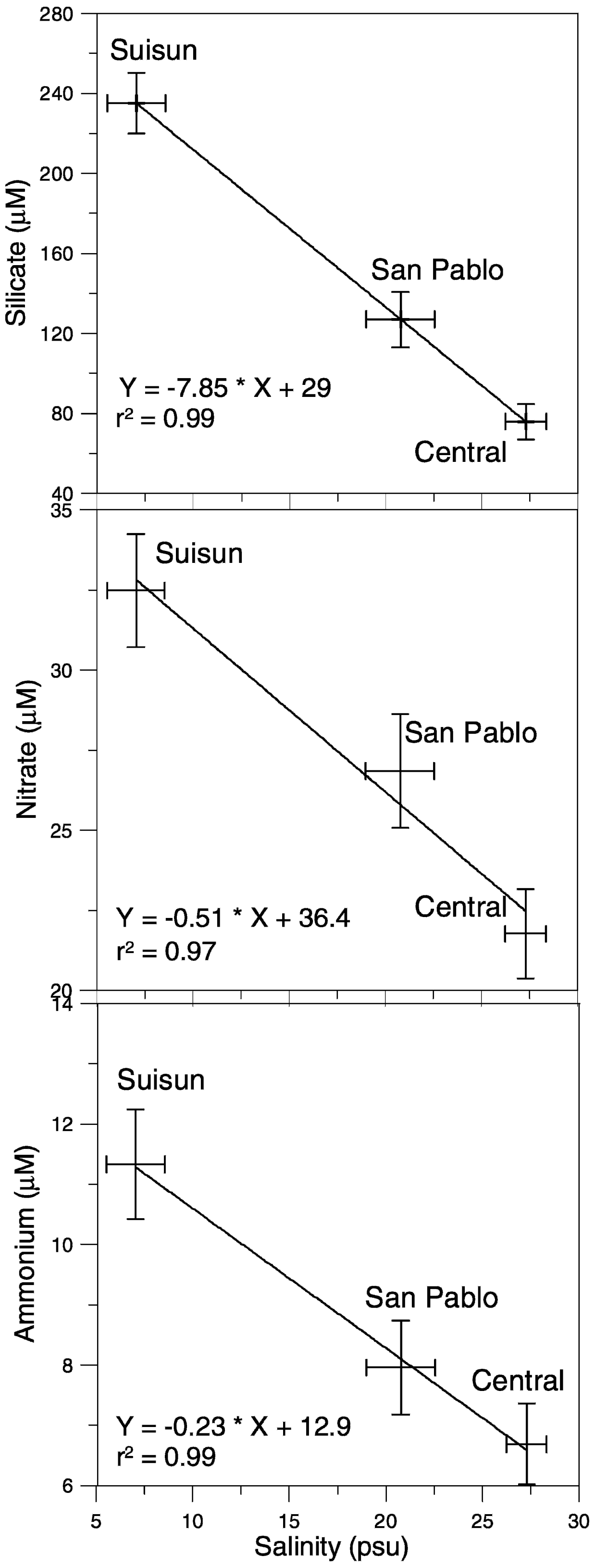

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Fig. 4. Mean nutrient concentration (±SE) for Suisun, San Pablo, and Central Bays versus mean salinity for all three years for the winter months (December, January, February), $Si(OH)_4$, NO_3, and NH_4.

also due to phytoplankton uptake, remaining relatively low or increasing slightly in summer and into fall. The spring minimum in NH_4 decreases in the seaward direction to below about 4 µM in Central and San Pablo Bays when NO_3 uptake (Fig. 6) then increases contributing to the spring bloom (Figs. 2 and 3). This does not happen in Suisun Bay where mean spring NH_4 values remain high (7 µM).

The mean values of VNO_3 for all three bays and all seasons plotted against NH_4 concentration (Fig. 6), show the values of VNO_3 to rise steeply as NH_4 concentrations are reduced to about 4 µM during spring bloom conditions. Sharp rises in mean VNO_3 from winter to spring occurred in parallel in both San Pablo and Central Bays. A much smaller increase is observed for Suisun Bay, where the mean spring value is driven by the one higher value from spring 2000. NO_3 uptake (as VNO_3) then decreases in all three bays from spring to summer and fall values. In contrast to VNO_3, all three bays show a much smaller increase in mean VNH_4 from winter to spring, a period of decreasing mean NH_4 concentration. Both San Pablo and Central Bays show large increases in VNH_4 from summer to fall when only small increases in mean NH_4 concentrations occur. Suisun Bay shows only one relatively small increase from spring to summer and has lower values of VNH_4 than the other two bays.

The ^{15}N uptake values can be used to calculate the f-ratio (an indicator of NO_3 to total DIN use), the ratio of $^{15}NO_3$ uptake (ρNO_3) to total DIN uptake (i.e., $\rho NO_3 + \rho NH_4$). The f-ratio is used here only to evaluate the relative use of NO_3 and NH_4, not to separate new and regenerated production as NO_3 and NH_4 have both new and regenerative sources in SFB. The plot of f-ratio versus NH_4 (Fig. 6), shows low values of about 0.2 in all bays and all seasons, except in spring when f-ratio values (based upon mean uptake values) increase to about 0.5, indicative of greater use of NO_3. These mean f-ratios representing percent NO_3 uptake (<0.5) in Table 2 and Figs. 6 and 7 do not reflect the true contribution of NO_3 uptake that occurs during these seasons since they average all conditions. For example, the nonaveraged data from San Pablo Bay (Fig. 2) yields a maximum f-ratio of 0.7 at the peak of the spring 2000 bloom (compared to the mean f-ratio for the spring of 0.35; Table 2). Mean chl *a* concentrations

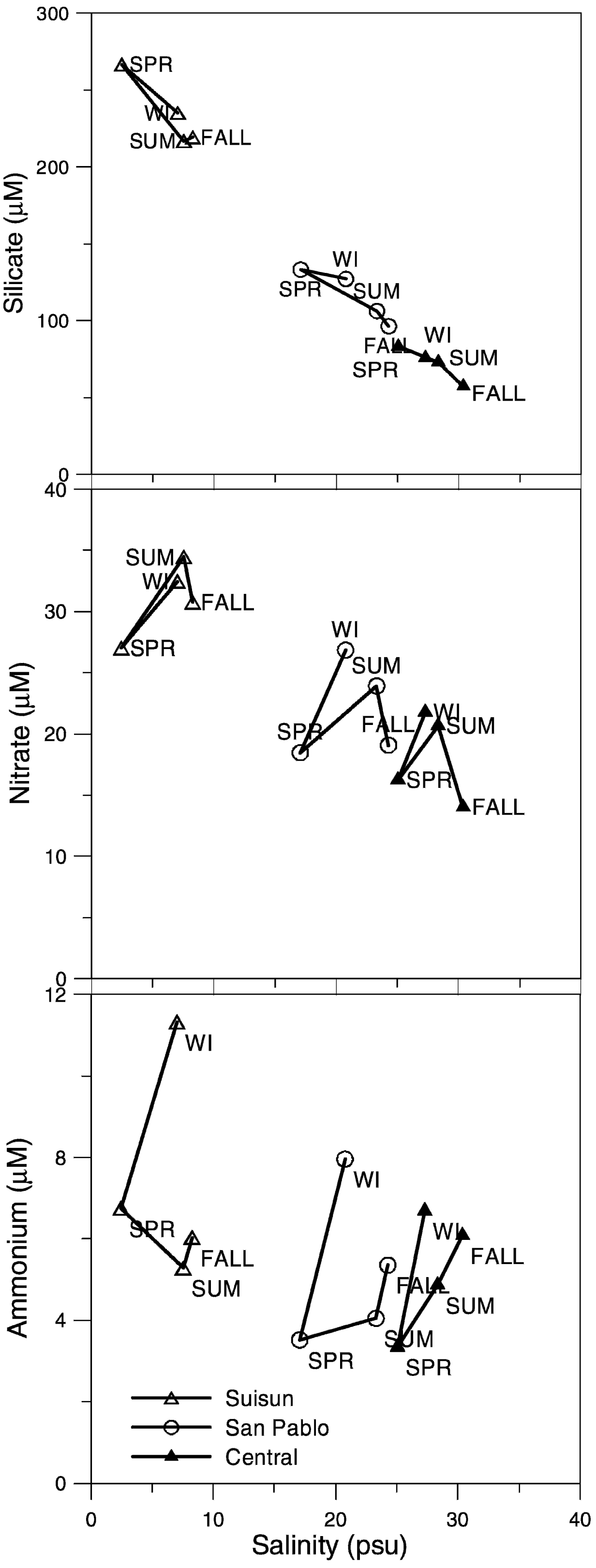

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Fig. 5. Mean nutrient concentration for Suisun, San Pablo, and Central Bays versus mean salinity for all three years for winter (WI), spring (SPR), summer (SUM), and fall (FALL) months, a) $Si(OH)_4$, b) NH_4, and c) NO_3.

(for the entire community) plotted against NH_4 concentration (Fig. 7) show parallel increases in all three bays from winter to spring values as NH_4 decreases. Suisun Bay has lower mean chlorophyll concentrations than San Pablo and Central Bays. All three bays show steep declines in chlorophyll from spring to summer. When plotted versus f-ratio, there is a linear relationship, with higher mean chlorophyll at higher mean f-ratios (i.e., NO_3 use) in the spring. Suisun Bay has lower nitrogen uptake and chlorophyll values than San Pablo and Central Bays at all seasons in the 3 yr mean data set (Figs. 6 and 7, Tables 1 and 2).

The mean data for nitrogen uptake can be used to estimate primary productivity as carbon uptake (Dugdale and Wilkerson 1992) by summing the mean ρNO_3 and ρNH_4 and multiplying by the Redfield ratio for carbon:nitrogen, 6.6 on a molar basis, multiplied by 12 to convert to mass units, and multiplied by 24 to give units of $\mu g\ C\ l^{-1}\ d^{-1}$ (Table 2). When carbon uptake values are plotted against mean f-ratios (Fig. 7), the seasonal cycles track the chlorophyll data and San Pablo and Central Bays can be seen to follow similar patterns with strong spring blooms at higher mean f-ratios (i.e., primary productivity based both on NO_3 and NH_4) and smaller, fall blooms at low f-ratios (based more on NH_4). Suisun Bay shows a small mean spring bloom, reduced primary production in summer, and no fall bloom. Suisun Bay differs from San Pablo and Central Bays in the lack of a fall bloom and a reduced spring bloom, and lower productivity that may be due to salinity stress or low irradiance conditions (Secchi values are shallower in Suisun compared to San Pablo and Central Bays; Figs. 1, 2, and 3, Table 1).

FRACTIONATED BIOMASS AND PRODUCTIVITY DATA

Biomass samples (as chl *a*) and nitrogen uptake-productivity measurements were obtained for the entire (total) phytoplankton community and also for the cells that were >5 μm in diameter, by using filters of 5 and 10 μm pore size to fractionate the samples. These data show that chl *a* concentration and NO_3 uptake are dominated by the larger cell sized population in all bays (Figs. 8 and 9) as the data all fall very close to the 1:1 line of fractionated versus total values. The chlorophyll data show good linear correlations (r^2 = 0.83 and 0.85) for regres-

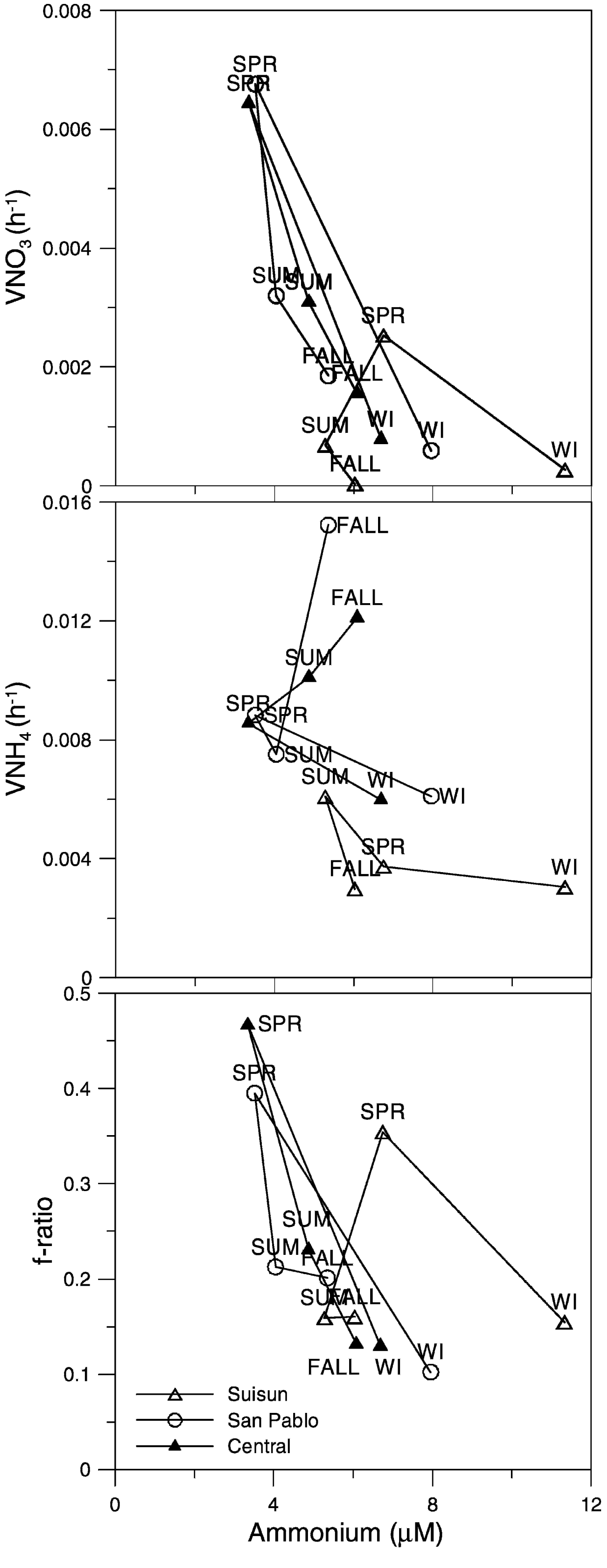

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Fig. 6. Mean NO_3 uptake (VNO_3), mean NH_4 uptake (VNH_4), and f ratio calculated as $\rho NO_3/(\rho NO_3 + \rho NH_4)$ for Suisun, San Pablo, and Central Bays versus mean NH_4 concentration for all three years for winter (WI), spring (SPR), summer (SUM), and fall (FALL) months.

sions of >5 µm and >10 µm cells versus chl *a*. The similarity in slopes between the chlorophyll in cells >5 µm versus total chlorophyll ($y = 0.84x - 0.64$) and chlorophyll in >10 µm cells versus total chlorophyll ($0.81x - 1.16$) regressions indicates that most of the larger cells are actually greater than 10 µm. The contribution by the larger cells is greatest at higher values of chlorophyll with an average of 90% of the total chlorophyll represented in the >5 µm cells at ambient chlorophyll concentrations of >10 µg l^{-1} (i.e., mean percentage of 90% for the 12 circled data points in Fig. 8).

NO_3 uptake (Fig. 9) shows an even tighter relationship between the larger cells and the total phytoplankton community with linear correlation, r^2 of 0.93 and slope of 0.84 suggesting that 84% of the time, uptake values measured were dominated by uptake in the larger cell size fraction. The dominance of the larger cells was greatest at the higher uptake rates, with larger cells contributing 87% of the total NO_3 uptake at values >0.2 µmol l^{-1} h^{-1} (i.e., mean of 7 data points circled in Fig. 9). This was not evident for the NH_4 uptake data that showed wide scatter in the data with the fractionated data not so close to the 1:1 line and a linear regression, r^2 of 0.64. The slope of 0.53 indicates that 53% of the values have uptake by cells >5 µm, i.e., both large and small cells are contributing to the uptake compared to the dominance by the larger cells in NO_3 uptake.

Discussion

All three bays in northern and central SFB exhibit high nutrients throughout the year with relatively low mean seasonal chlorophyll concentrations ranging from 1.2 to 6.5 µg l^{-1}. The specific NO_3 and NH_4 and uptake rates (and VNO_3 and $VNH_4 < 0.01$ h^{-1}) for most of the year are in the range of oligotrophic ocean values (Dugdale and Wilkerson 1992b). These conditions are essentially high nutrient low chlorophyll (HNLC; Cloern 2001) or high nutrient low growth (HNLG; Sharp 2001) known previously from open ocean studies (Minas et al. 1986). Primary nutrients are typically in excess of requirements and are exported from the estuary. Increase in biomass, i.e., phytoplankton blooms, occurs only with sudden bursts in growth rate, outpacing temporarily the losses, primarily grazing. These bursts result from an increase in NO_3 uptake

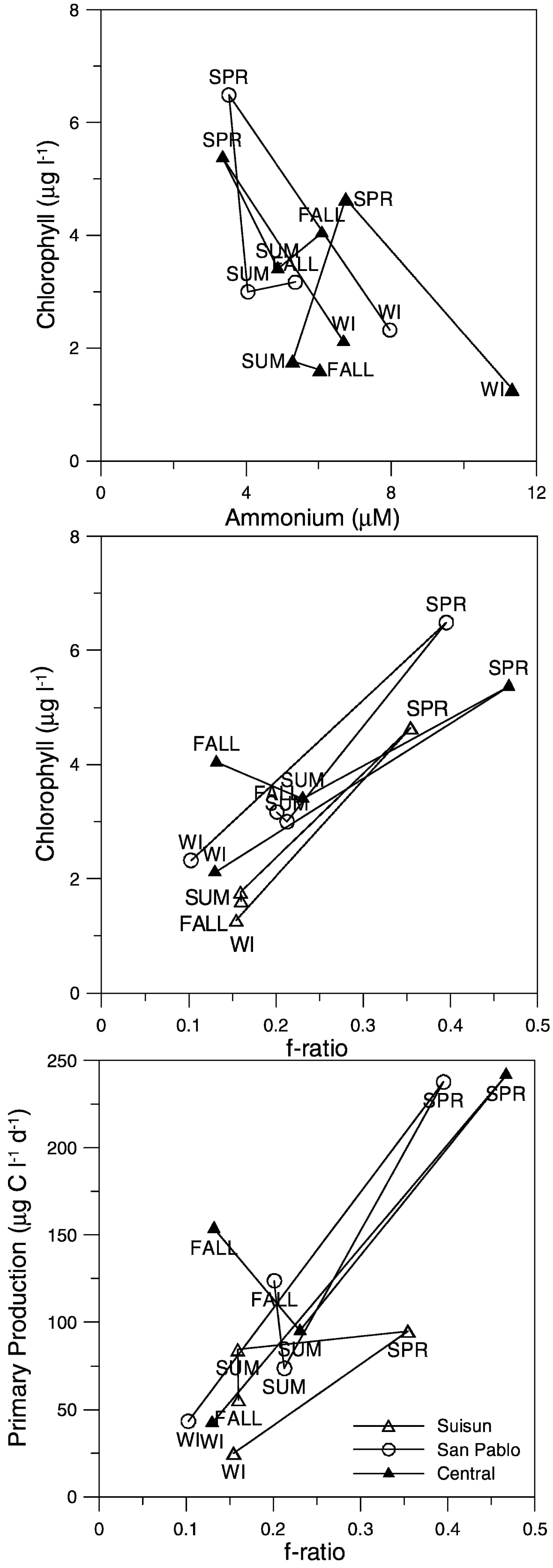

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Fig. 7. Suisun, San Pablo, and Central Bays for all three years for winter (WI), spring (SPR), summer (SUM), and fall (FALL) months, mean chlorophyll concentration versus mean NH_4 concentration and mean f ratio, mean calculated primary productivity versus mean f ratio.

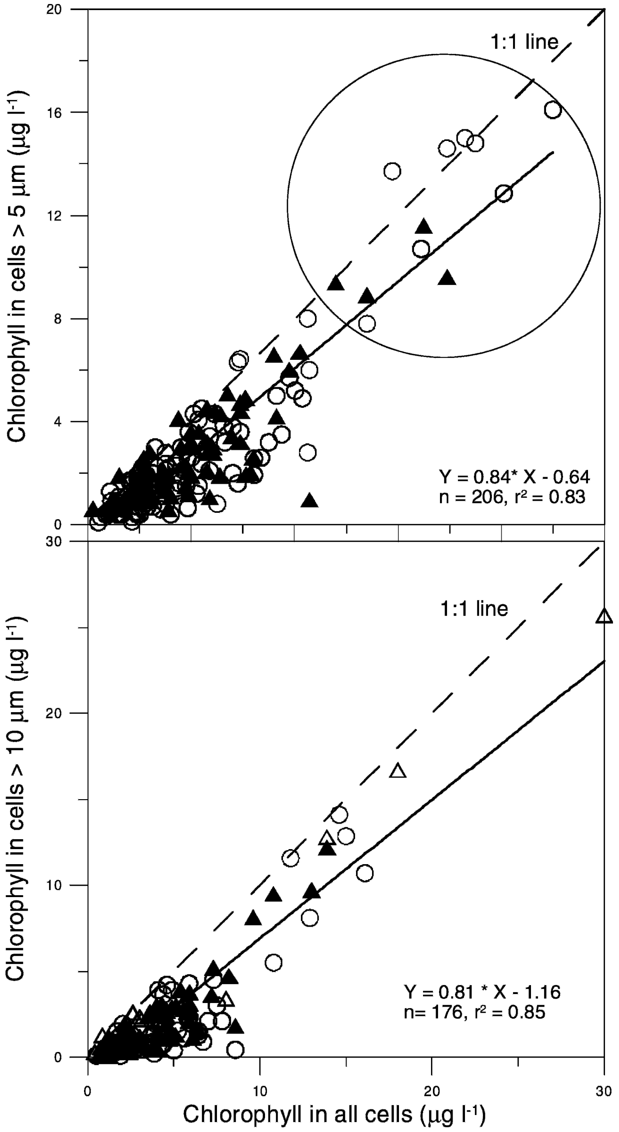

Fig. 8. Chlorophyll in cells >5 µm diameter and chlorophyll in cells >10 µm diameter versus total chlorophyll collected on a GF/F filter for all surface data collected between October 1999 and August 2003 from Suisun (circles), San Pablo (crosses), and Central (triangles) Bays. Linear regression and 1:1 relationship are indicated. Points within the circle are all values with total chlorophyll >10 µg l^{-1}.

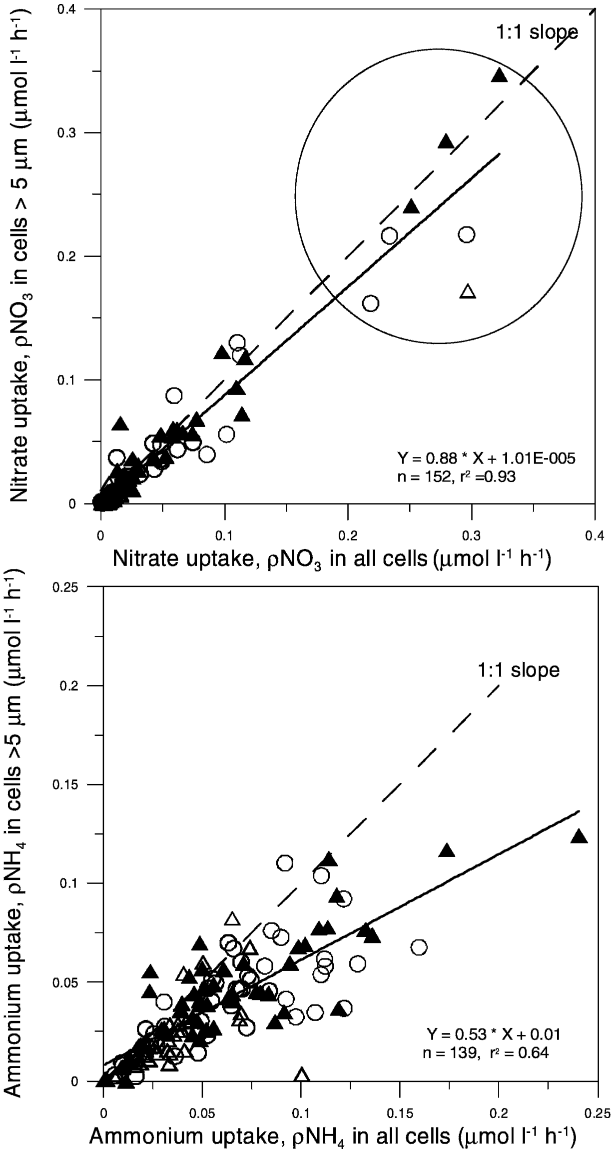

Fig. 9. NO_3 uptake by cells >5 µm diameter versus NO_3 uptake in all cells and NH_4 uptake by cells >5 µm diameter versus NH_4 uptake in all cells for all surface data collected between October 1999 and August 2003 from Suisun (circles), San Pablo (crosses), and Central (triangles) Bays. Linear regression and 1:1 relationship are indicated. Points within the circle are all values with ρNO_3 >0.2 µmol l^{-1} h^{-1}.

processes and are supported by access to the large NO_3 pool, but only occur when vertical salinity stratification improves the light conditions (e.g., in spring) and in the presence of low, noninhibitory concentrations of NH_4 (Figs. 1–3). Phytoplankton growth during most of the year is supported by NH_4 at relatively low growth rates (e.g., 0.013 h^{-1} in Central Bay in summer). These rates are likely held low by insufficient irradiance. When Central Bay water is enclosed and then exposed to ambient light, the VNH_4 rises rapidly to 0.03–0.05 h^{-1} indicating a primary light limitation (Dugdale unpublished data; Parker personal communication). Light limited low NH_4 based growth rate combined with relatively high NH_4 inputs to SFB results in high ambient NH_4 concentrations that would inhibit NO_3 uptake by the phytoplankton (e.g., Dortch 1990). Improved light conditions that result in higher VNH_4 should produce an increase in biomass, but only to the extent of the available

NH_4 pool, about 5 μM. If improved light conditions continue long enough at elevated NH_4 uptake rates, reducing ambient NH_4 concentrations below inhibiting levels, NO_3 uptake can begin with a biomass increase that is set by the much higher pool of NO_3, 20–30 μM.

From our ^{15}N measurements of nitrogen productivity, annual primary productivity in northern SFB can be separated into three seasons on the basis of nutrient processes: a spring bloom period dependent primarily on NO_3 uptake but initiated by NH_4 uptake, a quasi-steady state condition in summer with low productivity based primarily on NH_4, and a fall bloom period with chlorophyll increases lower than in spring and using primarily NH_4 as indicated by the low f-ratio, 0.13 to 0.2. Productivity performance in these seasons is also dependent on the position of the three northern bays in the salinity-nutrient gradient with higher nutrients and low salinity to the north and lower nutrients and high salinity to the south. The more southern San Pablo and Central Bays behave in relatively similar ways with strong spring phytoplankton blooms, weaker fall blooms, and lower mean nutrients and higher salinity. Suisun Bay separates out from these two on the basis of lower salinity, higher nutrients, and lower mean productivity (Tables 1 and 2). The lower productivity value is partly due to lack of spring blooms in Suisun Bay in 3 of the 4 yr studies here. This lack of spring blooms was likely a consequence of higher ambient NH_4 concentrations in Suisun inhibiting NO_3 uptake and by lower light availability.

Summer productivity in northern SFB, which tends to be much lower than the NO_3 fueled spring productivity (Cloern 1996), is based primarily on NH_4 as indicated by the low value of the f-ratio, 0.2 (Table 2). Mean phytoplankton growth rates for the summer calculated from the sum of specific NH_4 and NO_3 uptake rates are similar in San Pablo and Central Bays (0.011 and 0.013 h^{-1}, respectively) and lowest in Suisun Bay (0.007 h^{-1}; data from Table 2). Little change in NH_4 concentration occurs during summer, allowing a quasi-steady state condition to be assumed and the possible NH_4 inputs can be calculated from the NH_4 uptake data. Using Central Bay as an example, with mean summer of $\rho NH_4 = 0.038\ \mu mol\ l^{-1}\ h^{-1}$ and mean $NH_4 = 4.9\ \mu M$, the turnover time is 5.4 d (using a 24 h day for uptake), i.e., roughly 20% of the NH_4 in the dissolved pool is consumed and replaced daily from inputs. The gradient between bays is small in summer precluding significant net input from upstream, indicating that the NH_4 demand (i.e., phytoplankton uptake) is met by regeneration locally at the sediment interface (Caffrey 1995; Grenz et al. 2000), by grazing, or by sewage inputs from secondary treatment plants. The combination of inputs, losses, and the light field maintains the high NH_4 concentration that blocks access by the phytoplankton to the larger NO_3 pool. Sorting out the relative effects of these processes will require additional field work and modeling. The major element in the DIN regulation of productivity is the high NH_4 input and this is likely to be a major contributor to the cause of low seasonally integrated productivity in all three bays.

In other turbid estuaries with high NO_3 and high NH_4 conditions, low levels of NO_3 uptake have been reported. The mean specific nitrogen uptake rates for northern and central SFB (Table 2) are remarkably similar to those reported for a series of European turbid estuaries (Middelburg and Nieuwenhuize 2000a, their Table 2). The range of mean VNH_4 in SFB was 0.003–0.01 h^{-1} (winter–summer) compared to 0.004–0.012 h^{-1} reported for the Loire, and VNO_3 ranged from 0.0002 to 0.003 h^{-1} in SFB (winter–summer) compared to 0.0003–0.00275 h^{-1} in the Loire. The low NO_3 uptake rates in the European turbid estuaries result in export to the sea of most of the NO_3 entering or being produced in the estuaries; the same condition occurs in SFB for most of the year when phytoplankton blooms are absent.

The effect of climate, primarily through effects of precipitation on dilution of nutrient concentrations, on this seasonal variability is important. Mean spring salinities for the three bays were low in 2000, about half the values in the succeeding two years (2001 and 2002). The year 2000, based upon precipitation, was categorized by the California Department of Water Resources (http://cdec.water.ca.gov/cgi-progs/iodir/wsihist) as above normal and NH_4 concentrations in Suisun and San Pablo Bays were about half that of the following 2 yr, which were classified as dry. The effect of the above normal precipitation in 2000 on NH_4 concentration was to dilute it to below inhibitory levels and likely this contributed to the bloom that was observed in Suisun Bay that year, whereas in the dry years with less freshwater dilution and higher NH_4 concentrations, chlorophyll blooms were not observed. The wetter spring of 2000 resulted (through dilution) in lower NH_4 levels and higher phytoplankton NO_3 uptake and a chlorophyll peak in Suisun Bay. The other years were dry, NH_4 levels were high, NO_3 uptake was low, and no phytoplankton blooms were observed.

An alternative hypothesis to the role of NH_4 as the cause of low summer chlorophyll concentrations in Suisun Bay is grazing by the clam *C. amurensis*, as proposed by Cloern and Alpine (1991). To establish the role of the clam, grazing rates were compared to phytoplankton growth rates estimated from nitrogen assimilation data. In a balanced system, grazing rates require matching phytoplankton growth rates. Published pumping rates for the bivalve population imply a daily turnover of the entire water column (Cole et al. 1992; Werner and Hollibaugh 1993), i.e., a turnover rate of $1/24 = 0.04\ h^{-1}$. The mean summer surface growth rates in Suisun Bay of $0.007\ h^{-1}$ (i.e., sum of VNO_3 and VNH_4) are an order of magnitude less than the calculated turnover rate for the water column used here as a proxy for clam grazing. The value of the phytoplankton growth rate would be even lower if calculated on a depth integrated basis. This suggests that the clam and phytoplankton populations are not in equilibrium and the role of clam grazing may not be the universal cause of the lower phytoplankton production and growth rates. The similarity of the mean specific NH_4 uptake rates in summer in the three bays, even though significant populations of *C. amurensis* have not been observed in Central Bay (Thompson personal communication), also argues against a simple bivalve grazing-phytoplankton growth system during summer. The clam population is also at a minimum in Suisun and San Pablo Bays during the spring bloom period and is unlikely to be a major factor in the difference between spring productivities in Suisun versus San Pablo and Central Bays.

The elevated chlorophyll levels making up the blooms in the northern and central parts of SFB are made up predominantly by larger cells, as illustrated by the high percentage of chlorophyll in cells $>5\ \mu m$ in diameter making up the population (Fig. 8, Table 1). This matches studies of eutrophic areas that are capable of supporting blooms that develop with the addition of large size classes (e.g., Malone 1980; Raimbault et al. 1988; Chisholm 1992) and thrive under conditions of high nutrients (e.g., Tamigneaux et al. 1995). It was previously described for SFB by Cloern and Dufford (2005) who observed that cells $<8\ \mu m$ contributed only 40% of community biomass and by Hogue et al. (2001) who showed dominance by large cells during the spring bloom period. NO_3 uptake in SFB also showed significant contribution by the larger cell sized phytoplankton (linear regression of all surface data indicating that 84% of uptake was due to cells $>5\ \mu m$; Fig. 9). A similar analysis made for phytoplankton in the upwelling area of Monterey Bay that has high NO_3 concentrations and uptake rates showed similar relationships (Wilkerson et al. 2000), with 87% of the total phytoplankton NO_3 uptake dominated by larger cells and with larger cells contributing 60% to the total chlorophyll. Interestingly in the Thames estuary where NO_3 is extremely high ($650\ \mu M$), very small cells, i.e., bacteria, were responsible for most of the NO_3 uptake (Middelburg and Nieuwenhuize 2000b).

When nitrogen productivity in northern SFB is sufficient for biomass to be built up and exceed grazing and other loss factors, then the phytoplankton contributing most to the process are larger cells. This is the case for the spring blooms in all three bays studied here. In SFB these larger phytoplankton are likely to be diatoms especially *Skeletonema costatum*, *Chaetoceros* species, *Thalassiosira* species, and *Coscinodiscus* (Cloern and Dufford 2005). Diatoms thrive in the high NO_3 environments, have inherently high growth rates, and are well suited to be the dominant functional group as reviewed by Cloern and Dufford (2005). Consequently, alleviating any HNLC-HNLG condition in SFB leading to higher NO_3 utilization should lead to a healthy food chain based upon larger cells (Fig. 8), likely diatoms, rather than driving the system towards more typical results of added nutrients or eutrophication as classically described in east coast estuaries, i.e., anoxia and harmful algal blooms (e.g., Sharp 2001; Hallegraeff 1993). The fall bloom in SFB, apparently supported more by NH_4 uptake (e.g., Figs. 2 and 3), is not dominated by larger cells, but by smaller cells (Fig. 9), most likely flagellates. These typically do not include toxic dinoflagellates in SFB (Cloern and Dufford 2005), although some harmful algal members have been observed episodically. For example blooms of *Heterosigma akashiwo* were observed in Richardson Bay (Herndon et al. 2003) and an anomalous unprecedented red tide in Central Bay of *Akashiwo sanguinea* (= *Gymnodinium splendens*) was observed in September 2004, that reduced NO_3 and NH_4 to some of the lowest concentrations measured (Cloern et al. 2005a,b).

This extensive time series data shows the HNLC-HNLG condition of northern SFB overlaid with regular seasonal increases in phytoplankton and their nitrogen assimilation rates. The primary production environment of SFB should be viewed as primarily light limited in which suboptimal light conditions hold phytoplankton growth rates low. Bursts of productivity (blooms) occur with periods of favorable light conditions, especially those that last for sufficient length of time to reduce NH_4 concentrations to levels allowing access to the larger NO_3 pool. The frequency and strength of these events, secondarily controlled by NH_4 and NO_3 interactions, are likely to have a strong influence on the integrated annual phytoplankton production. The effect of water management changes, i.e., changing DIN loading, can now be modeled using these nitrogen productivity data as a framework to understand the importance of different nutrient concentrations in the development of phytoplankton blooms in the northern SFB.

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Sources of Unpublished Materials

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