Long-term changes in apparent uptake of silica in the San Francisco estuary

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Abstract

Silica distributions in estuaries can be used to infer uptake, particularly that due to production by diatoms. I used data from two long-term monitoring programs to infer long-term patterns of diatom production during summer in the river-dominated northern San Francisco estuary. This region was most heavily affected by grazing by the clam *Potamocorbula amurensis,* introduced in 1986. Production based on dissolved silica (Dsi) uptake was high during the 1970s and early 1980s except during a drought in 1976–1977. From 1987 to 2002 production averaged 1% and 17% of the preclam values from the two monitoring programs. Low values in 1976–1977 and after 1986 are consistent with a loss of diatom production due to benthic grazing. There is no evidence of a relation between DSi-based production and either freshwater flow or temperature, and therefore climate change is an unlikely influence on the long-term trend in diatom production in this part of the estuary. Primary production calculated from chlorophyll and extinction coefficient was of a similar magnitude to that calculated from DSi depletion, indicating that most production was due to diatoms during summers of the preclam period.

The supply, removal, and use of nutrients are key processes in aquatic ecosystems. Dissolved silica (DSi) is particularly useful in biogeochemical studies because it is taken up predominantly by diatoms, has a relatively low remineralization rate, and enters natural waters primarily through weathering of rocks. Recent work has refined global estimates of Si transport (Nelson et al. 1995), revealed the importance of DSi in regulating new production in upwelling regions (Dugdale and Wilkerson 1998), and suggested alternative functions of the Si tests of diatoms (e.g., Milligan and Morel 2002).

Patterns of use of DSi can be informative, particularly in estuaries. Blooms by nondiatom phytoplankton can result from DSi depletion when other nutrients are anthropogenically enhanced (Officer and Ryther 1980). A useful way to examine DSi distributions in estuaries is through the use of mixing diagrams (Officer and Lynch 1981). Because of the limited rate of remineralization and unambiguous source term, mixing diagrams can show clearly when uptake is strong and when DSi is relatively conservative (Peterson et al. 1985). Generally, high freshwater flow and low temperature and solar radiation result in domination of the DSi distribution by mixing. Under conditions of low flow and high solar radiation and temperature, DSi concentration is depressed through uptake by diatoms (Peterson et al. 1985). Since DSi depletion results from uptake integrated over a period of time it can be a useful and inexpensive indicator of integrated diatom production.

I re-examined the distribution of DSi in the northern San Francisco estuary following the approach of Peterson et al. (1985). Summer conditions in the northern San Francisco estuary, particularly Suisun Bay (Fig. 1), are ideal for examining the role of DSi. Consistently low river flow leads to long residence time (Walters et al. 1985), and therefore to conditions near steady state, and summer is the time of highest phytoplankton growth rate (Cole and Cloern 1984). Previous analysis showed high DSi depletion during most summers except during an extended drought in Suisun Bay in 1976–1977, when low river flow and benthic grazing suppressed phytoplankton biomass and therefore uptake (Nichols 1985; Peterson et al. 1985). Phytoplankton biomass in Suisun Bay decreased sharply in 1987, apparently because of grazing by the introduced clam *Potamocorbula amurensis* (Alpine and Cloern 1992). I show a similar reduction in the estimated rate of DSi uptake.

Methods

Data on DSi concentration, chlorophyll, and various measures of light penetration were obtained from two monitoring programs. The U.S. Geological Survey (USGS) has conducted surveys, many including the northern estuary, approximately monthly since 1969 with some gaps (http://sfbay.wr.usgs.gov/access). Surveys, which included up to 20 stations in the northern estuary (Fig. 1), were usually conducted in 1 d, although some surveys took 2 d to complete. Near-surface samples, and up to six deeper samples at some stations, were taken at each station for nutrient concentrations, which were determined with a Technicon Autoanalyzer. Hager (1993) described details of the method including quality-control procedures and results.

Ancillary data collected at each station included temperature, salinity, suspended particulate matter (SPM, mg L^{-1}), light extinction coefficient, and chlorophyll determined by in vivo fluorescence calibrated against extracted chlorophyll measurements (Cole and Cloern 1984). Extinction coefficient was filled in for 3,751 samples of 11,023 using a linear regression of extinction on SPM: extinction $= 0.8 + (0.050 \pm 0.005)$ SPM (95% confidence limits [CL]), 5,127 degrees
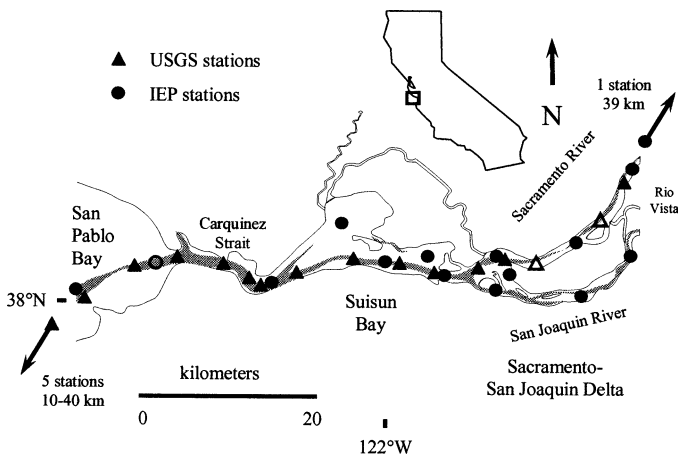
Fig. 1. Map of the study area showing USGS stations and IEP stations. Open symbols represent stations visited on fewer than half of the surveys. Arrow at the left indicates that five USGS stations were 10–40 km further seaward than the stations indicated here. Arrow at the right indicates one IEP station further up the Sacramento River. Gray shading indicates the 10-m depth contour.

of freedom, and the standard deviation of residuals was 0.7 m^{-1}.

The Interagency Ecological Program (IEP) (http://www.iep.water.ca.gov) has conducted surveys once or twice monthly since 1975 in the northern estuary, emphasizing the Sacramento–San Joaquin Delta (Fig. 1). Each survey took several days to complete. Samples were collected with submersible pumps with plastic or stainless steel impellers, filtered, and stored at 4°C for analysis. DSi was analyzed using three methods over the course of the study, all by the Department of Water Resources' (DWR) Environmental Protection Agency (EPA)-certified laboratory. USGS method I-1700-85 was used from 1975 to February 1994, standard method 4500-Si-D until July 1997, and EPA method 200.7 since then. The first two are colorimetric methods using molybdate blue. Under the latter method samples were acidified for storage, and analyzed using an inductively coupled plasma emission spectrometer (ICP) calibrated with $(NH_4)_2SiF_6$. Standard curves were run for each set of analyses for all three methods. There was no explicit comparison of results among the different methods. However, until 1996 the DWR laboratory participated in the USGS's semiannual laboratory calibration, which showed that the colorimetric and ICP methods give comparable results (e.g., Farrar and Long 1996), and in which the DWR lab usually got values within 1 standard deviation of the mean for DSi from all participating laboratories.

DSi was reported as mg L^{-1} SiO$_2$, which I converted to μmol L^{-1} using a molecular weight of 60. Ancillary data included extracted chlorophyll, specific conductance, secchi depth, and on 4,640 occasions (of a total of 11,502 sampling events), depth of the 1% light level. Chlorophyll was determined by spectrophotometry after extraction in acetone. Salinity in practical salinity units was computed from specific conductance using the equation of state of seawater. Depth of the 1% light level was converted to extinction coefficient k (m^{-1}), which was estimated for all samples by regression

on 1/secchi depth (m). Because variance of the data was heterogeneous I used a generalized linear model with linear link function and variance proportional to the mean squared. The resulting regression was $k = 0.36 + (0.60 \pm 0.01) /$ secchi (95% CL), 4,638 degrees of freedom, and the standard deviation of residuals was 0.47 m^{-1}.

In both surveys stations were occasionally missed and some stations were unsuitable for inclusion. Stations were included from the northern estuary including Central San Francisco Bay (USGS only), San Pablo Bay, Suisun Bay, and the northern Sacramento–San Joaquin Delta along the Sacramento River or on the San Joaquin River within a tidal excursion of the confluence. Since nearly all of the river flow in summer comes down the Sacramento River, this provided transects from high-salinity water to the freshwater source without including stations in the central and southern Delta (IEP only), a freshwater region with long residence time in summer. Surveys were used in the analysis if they included at least five stations, of which at least two were landward of Suisun Bay, and the salinity range was <1 to >20.

Primary production was calculated using the model of Cole and Cloern (1984) with parameters determined by Jassby et al. (2002):

$$P_s = 4.61\phi BI_0/k$$

where P_s is gross primary productivity (mg C m^{-2} d^{-1}), ϕ is an efficiency factor, B is chlorophyll concentration (mg m^{-3}), I_0 is surface photosynthetically active radiation (E m^{-2} d^{-1}), and k is the extinction coefficient (m^{-1}). Jassby et al. (2002) reported an estimate of $\phi = 0.73 \pm 0.023$ mg C (mg Chl a)$^{-1}$ (E m^{-2})$^{-1}$ ($R^2 = 0.952$, $p = 0.001$) based on 51 samples taken in the Sacramento–San Joaquin Delta in 1997.

Irradiance data were obtained from the Integrated Pest Management site at UC Davis, about 60 km northeast of Suisun Bay (http://www.ipm.ucdavis.edu/weather/wxretrieve.html). Data were converted from daily mean watts m^{-2} to quanta by a factor 0.18 mol quanta d^{-1} watt^{-1} (Morel and Smith 1974).

DSi uptake was calculated according to the steady-state model of Officer and Lynch (1981 Eq. 39). The approach is to determine the fluxes of DSi past two points defined by salinity, generally one near freshwater and one at a higher salinity, and calculate their difference. Flux at a point can be determined by the y-intercept of a mixing curve of DSi versus salinity at that point, divided by the hydraulic residence time, which is the volume of the region of interest divided by the freshwater flow. Thus DSi uptake (μmol L^{-1} d^{-1}) is:

$$\rho_{Si} = \frac{(y_2 - y_1)Q}{V}$$

where y_1 is the y-intercept (μmol L^{-1}) for data from low salinity, y_2 the y-intercept for data from high salinity, Q the freshwater flow rate, and V the volume. Volume was taken to be that from the western margin of Suisun Bay to the confluence of the Sacramento and San Joaquin Rivers, 562 × 10^6 m^3 (http://sfbay.wr.usgs.gov/access/Bathy). This distance is about 25 km, which is approximately the median distance between stations at 0.5 and 10 salinity. Freshwater flow was obtained from the Dayflow water accounting system
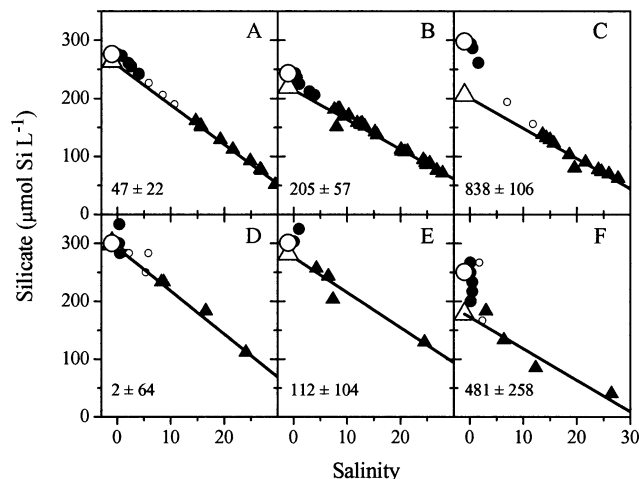
Fig. 2. Examples of mixing curves for DSi selected at random from the range of values of estimated DSi uptake: (A, D) lower third of uptake value; (B, E) middle third; and (C, F) upper third of data from USGS (A, B, C) and IEP (D, E, F) surveys. Solid triangles, data used to calculate the intercept for high salinity; filled circles, data used to calculate the intercept for low salinity; open circles, remaining points if any; line, robust fit to the filled triangles showing intercept for high salinity as large open triangle; large open circle, intercept for low salinity. Intercept symbols shifted one unit left to make data points visible. Numbers in lower left of each panel give the mean and 95% confidence interval for estimated DSi uptake expressed as primary production (mg C m^{-3} d^{-1}) based on the data in that panel.

(Net delta outflow, http://www.iep.water.ca.gov/dayflow). Water temperature at a continuous monitoring station at Freeport on the Sacramento River was also obtained from IEP.

Most of the mixing curves had regions of fairly constant slope at salinity above ~10, making the slope robust at that point. However, in some cases there were apparent outliers, so I used robust regression (function rlm in S-Plus) to prevent outliers from unduly influencing the intercepts. Often the slope at low salinity was difficult to determine because of sharp changes in DSi concentration over small ranges of salinity (corresponding to distances of tens of kilometers). However, the *y*-intercept was constrained mainly by the values at the lowest salinity and was therefore insensitive to the slope of the line fitting the data. DSi uptake (μmol L^{-1} d^{-1}) was converted to production assuming a C : Si molar ratio of 6.6, although variability in this ratio (Claquin et al. 2002) likely leads to error variance in the converted data.

Temporal changes in DSi uptake were analyzed using regression trees constrained to a single split between an earlier and later period. Once the timing of the split had been determined the magnitude of the change was determined by linear regression using a binary variable (0 before, 1 after the split) as the covariate. Residuals had no time trend and graphical examination indicated that assumptions of the linear regression had been met.

Results

In all, 40 surveys from the USGS and 147 from the IEP met the criteria to be included. Examples of mixing curves
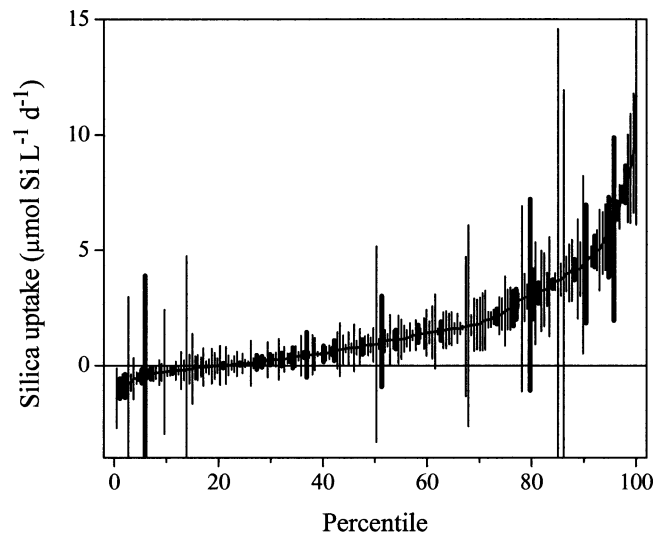

Fig. 3. Cumulative distribution of DSi uptake estimates for both sources. Heavy error bars indicate USGS data; thin error bars, IEP data.

were drawn at random from the lower, middle, and upper third of the DSi uptake values from each data set (Fig. 2). On some occasions either there was no upward curvature or the data were too variable to detect it (e.g., Fig. 2D), whereas on others the curvature was prominent and focused at salinity between ~1 and 10, and the fits of the lines reasonable (e.g., Fig. 2C). In most instances confidence limits around the calculated DSi fluxes were relatively small, so that 60% of the calculated fluxes were greater than zero (Fig. 3). Negative estimated fluxes occurred because of slight negative curvature at salinity ~15–20, or on some occasions because of apparent outliers that distorted the fits of the lines even with the use of robust regression. DSi concentrations at low salinity based on the intercepts had a mean of 280 μmol L^{-1} and a coefficient of variation of 13% for both data sets pooled.

Long-term trends of DSi uptake indicated a step change after 1986 in both data sets, and considerably more variability before than after that time (Fig. 4). The IEP data also showed low values during 1976–1977. The timing of the step for the USGS data set was uncertain because no data were collected in the northern estuary between 1984 and 1988. Furthermore, the magnitude of the step for the USGS was elevated by the high value for 1969, from which only one survey met the criteria to be included.

Freshwater flow during the same period showed no time trend and no step change (graphical analysis and linear and tree regression, $p > 0.1$), and was characterized by high interannual and decadal variability (Fig. 5A). In particular, droughts in 1976–1977 and 1987–1992 and floods in 1982–1983, 1995, and 1998 are prominent. Summer temperature showed no long-term trend and little variation (Fig. 5B). The short-term time trend in freshwater flow in the 30 d leading up to each sampling event was slightly negative in June ($-6.6\% \pm 3.6\%$ d^{-1}, slope with 95% CL) but not during later months ($-1.5\% \pm 1.8\%$ d^{-1}).

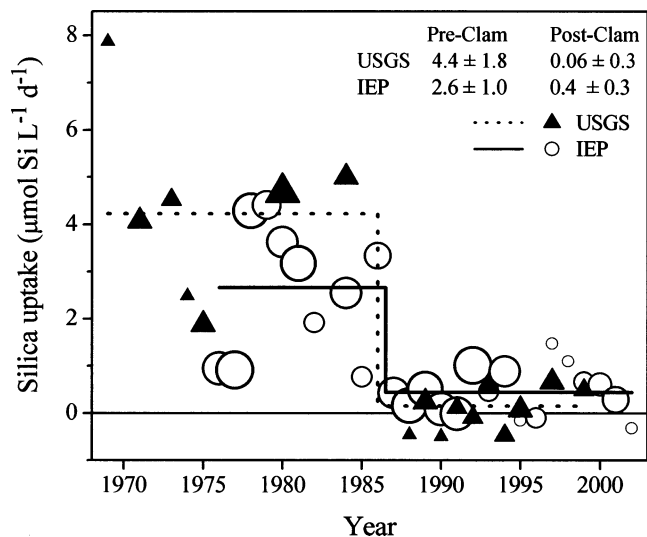Production estimated from light and chlorophyll and pro-

Fig. 4. Annual DSi uptake rates, annual means weighted by the number of surveys included, proportional to area of symbols and ranging from 1 to 10 surveys. Lines are from regression trees fit to the data and constrained to one split of the data. Numbers in legend are production estimates ± 95% CL for the period before ("Preclam") and after ("Postclam") the break.
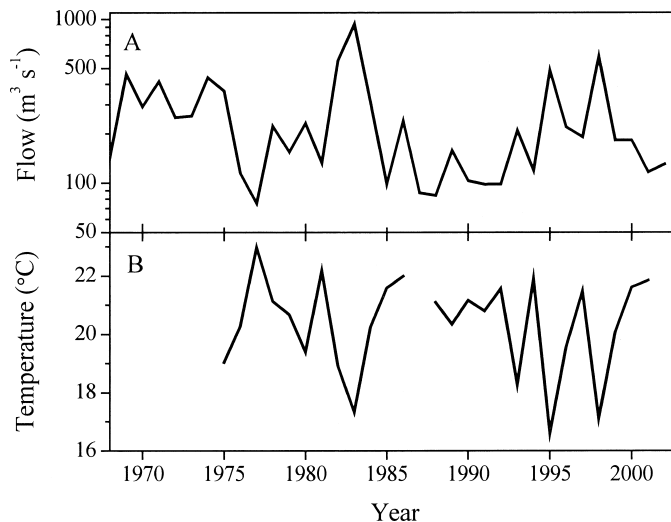

Fig. 5. (A) Annual mean summer freshwater outflow, and (B) temperature for June. Temperature is from a continuous monitoring station at Freeport near Sacramento.

duction estimated from DSi uptake both occurred in two clusters for both data sets, one cluster through 1986 and the other from 1987 on, with strong correlations between the two alternative estimates (Fig. 6). The Si-based production values from the USGS data were much higher than those based on chlorophyll from the preclam period. Because of missing data, these preclam data points were all from 1980. Production based on chlorophyll exceeded that based on DSi in the IEP data set for the period 1975–1986 by 54 ± 47 mg C m^{-3} d^{-1}.

Discussion

Previous studies have shown increasing nutrient concentrations caused by filtration of phytoplankton by introduced bivalves, most notably the zebra mussel (Caraco et al.1997). In some cases the changes in nutrient concentrations or cycling may increase growth rates and quality of phytoplankton as food for herbivores (Prins et al. 1998). Increasing nutrient concentrations are less likely to stimulate phytoplankton growth in the northern San Francisco estuary because nutrients, particularly DSi, are rarely limiting (Cloern et al. 1983).

Two key assumptions underlie the estimates presented here. First, the model used to estimate uptake assumes steady state (Officer and Lynch 1981), which may not always apply, especially at high and varying river flows. DSi concentrations were measured daily during three 2–3-month time periods during 1983–1984 in the Sacramento River at Rio Vista (Fig. 1; Schemel and Hager 1986). Concentrations were remarkably steady, with coefficients of variation of 8% and 9% during two high-flow periods and 5% during a low-flow period; mean concentrations were 248, 251, and 267 μmol L^{-1} respectively (Schemel and Hager 1986). These values

are close to the mean from this study for the low-salinity intercept of 280 μmol L^{-1}, which had a slightly larger coefficient of variation (13%) presumably due to the longer and more variable study period, but which still indicated a relatively stable source concentration.

During the winter high-flow period nutrient concentrations in the northern San Francisco estuary are controlled by hydrology (Schemel et al. 1984), and mixing models show conservative behavior of nutrients because of both high turnover and low uptake rate (Peterson et al. 1985). Water residence time in Suisun Bay in summer is ~35 d at a low flow of 100 m^3 s^{-1} and 0.5 d at 10^4 m^3 s^{-1} (Walters et al. 1985). Median flow in the data used here was 136 m^3 s^{-1}, and the 90th percentile was 383 m^3 s^{-1}. If residence time scales as the inverse of flow, the median residence time would have been ~26 d. By comparison, the timescale for DSi uptake rate (i.e., concentration/uptake) during the preclam period had a median of 37 d.
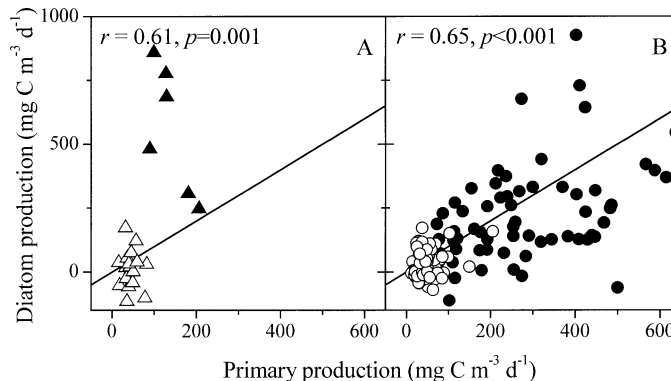

Fig. 6. Primary production calculated from chlorophyll versus that calculated from DSi anomalies, with 1 : 1 lines. (A) USGS data; (B) IEP data. Closed symbols, data through 1986; open symbols, after 1986. Note that the USGS data for the preclam period are from 1980 only.

These calculations imply that the steady-state assumption was valid only part of the time. Violation of this assumption would result in error variance unless freshwater flow had a consistent short-term time trend, either up or down, during the sampling events. The trend in flow was slightly negative on average, particularly in June, reflecting the declining hydrograph in the transition from the spring high-flow period to the dry season. This would introduce some bias to those values, but there was no relation between the flow trend and the difference in intercepts on the mixing curves. To some extent the added error variance was removed by averaging, i.e., where the data points in Fig. 4 represent more than one survey. Remaining error variance showed up as unexplained variance in the analysis of the annual trend, which was nevertheless highly significant.

The second assumption is that remineralization rates of Si are slow compared to uptake and mixing rates. Production calculated from DSi is essentially net ecosystem production and therefore conceptually distinct from gross production by diatoms. However, if remineralization is slow, DSi uptake is equivalent to gross primary production.

The assumption of slow remineralization in studies of DSi fluxes may not be strictly correct. Benthic grazing, which is high in the study area (Alpine and Cloern 1992), can increase the rate of Si remineralization (Chauvaud et al. 2000). Remineralization was inferred as an important term in the Si budget under the Danube River outflow plume (Ragueneau et al. 2002). In the Monterey Bay upwelling area, the ratio of DSi uptake to dissolution was high during blooms and declined between blooms (Brzezinski et al. 2003).

The effect of a nontrivial remineralization rate would be to raise DSi concentrations above the values due to sequestration of Si, i.e., either to flatten the curvature of the mixing diagrams, or to add negative (concave-downward) curvature at some other salinity, depending on where the remineralization occurred. Either way, substantial remineralization would result in underestimates of gross DSi-based production. Yet, the DSi-based production values were generally comparable to production calculated from chlorophyll (Fig. 6). Note that these values were based on an assumption that most of the production occurred in Suisun Bay, with mid-tide volume of 562 ± 10^6 m^3. Because the region of DSi uptake cannot be resolved from the data used for the mixing diagrams, this value is uncertain, so the absolute values of DSi-based production have an unknown bias. Additional bias and variability arises because the C:Si ratio likely varies from the value used of 6.6 (Claquin et al. 2002). The most accurate statement is therefore that the two measures of production have a similar magnitude, but that the relationship between them cannot be specified precisely.

Abundance of *P. amurensis* was above 10^3 m^{-2} in Suisun or San Pablo Bays or both during summers of every year beginning in 1987 (Kimmerer 2004). Although biomass or filtration rate figures are not available for the period of this study, estimates of mean annual clam respiration during 7 yr exceeded estimates of mean annual primary production (Chauvaud et al. 2003), indicating that the clams were consuming more organic carbon than the phytoplankton produced. High bivalve abundance before 1987 was recorded only during a drought in 1976–1977, when chlorophyll was reduced by benthic grazing (Nichols 1985).

Previous analyses have demonstrated that chlorophyll concentrations in Suisun Bay (Kimmerer 2004) and the western Sacramento–San Joaquin Delta (Jassby et al. 2002) declined during late springs and summers after 1986. Diatom biovolume throughout the entire northern estuary declined in the late 1980s but recovered by 1993 to its long-term mean (Lehman 2000). However, this analysis included the entire Delta, which is largely a tidal freshwater region. The effect of *P. amurensis* on phytoplankton in the Delta is limited to the western region, and chlorophyll concentration in the Delta as a whole has modes of variation not seen in Suisun Bay (Jassby et al. 2002). Lehman (1996) reported a decrease in diatom abundance at stations in Suisun Bay following the introduction of *P. amurensis*. A decline in the proportion of diatoms in the phytoplankton is a reasonable response to bivalve grazing, since filtration efficiency of bivalves drops below a particle size of about 2–3 μm (Winter 1978), so that most diatoms, but not nanophytoplankton, would be captured efficiently.

Counting and estimating biomass or volume of phytoplankton is difficult in a matrix rich in detrital matter, and does not allow calculation of production. The DSi depletion results indicate that most of the production in the northern estuary before 1987 was by diatoms. Furthermore, there is no indication that the decline in diatom production was related to climate, which is most likely to influence this river-dominated reach of the estuary through freshwater flow. Neither temperature nor freshwater flow had long-term trends or step changes during the time period of this study; although flow was low from 1987–1992, the recovery of flow in the mid 1990s did not result in a recovery of DSi uptake. Rather, the decline of DSi uptake in 1986–1987, as well as the brief period of low DSi uptake and phytoplankton biomass in 1976–1977 (Nichols 1985; Peterson et al. 1985), are most likely the result of elevated benthic grazing.

Although negative effects of diatoms on copepod production have been reported, these effects were not found in a more recent effort, and the traditional view of an estuarine or marine food web based substantially on diatoms still holds (Irigoien et al. 2002). Indeed, the high growth rate of diatoms and their large size ensures their substantial contribution to higher trophic levels in most coastal and estuarine systems. Losses of diatom production occurring when the atomic dissolved Si:N ratio fell below 1:1 have been blamed for a reduction in ability of coastal food webs to support higher trophic levels (Turner et al. 1998). In the San Francisco estuary, numerous changes have been noted in the abundance and species composition of pelagic consumers (Kimmerer 2004), most of which cannot consume small cells directly. Changes in the consumer assemblage are likely due to the decline in phytoplankton, particularly that in the larger cells such as diatoms.

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