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# High nutrient pulses, tidal mixing and biological response in a small California estuary: Variability in nutrient concentrations from decadal to hourly time scales

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**Abstract**

Elkhorn Slough is a small estuary in Central California, where nutrient inputs are dominated by runoff from agricultural row crops, a golf course, and residential development. We examined the variability in nutrient concentrations from decadal to hourly time scales in Elkhorn Slough to compare forcing by physical and biological factors. Hourly data were collected using in situ nitrate analyzers and water quality data sondes, and two decades of monthly monitoring data were analyzed. Nutrient concentrations increased from the mid 1970s to 1990s as pastures and woodlands were converted to row crops and population increased in the watershed. Climatic variability was also a significant factor controlling interannual nutrient variability, with higher nutrient concentrations during wet than drought years. Elkhorn Slough has a Mediterranean climate with dry and rainy seasons. Dissolved inorganic nitrogen (DIN) concentrations were relatively low (10–70 μmol $L^{-1}$) during the dry season and high (20–160 μmol $L^{-1}$) during the rainy season. Dissolved inorganic phosphorus (DIP) concentrations showed the inverse pattern, with higher concentrations during the dry season. Pulsed runoff events were a consistent feature controlling nitrate concentrations during the rainy season. Peak nitrate concentrations lagged runoff events by 1 to 6 days. Tidal exchange with Monterey Bay was also an important process controlling nutrient concentrations, particularly near the mouth of the Slough. Biological processes had the greatest effect on nitrate concentrations during the dry season and were less important during the rainy season. While primary production was enhanced by nutrient pulses, chlorophyll *a* concentrations were not. We believe that the generally weak biological response compared to the strong physical forcing in Elkhorn Slough occurred because the short residence time and tidal mixing rapidly diluted nutrient pulses.


*Keywords:* nutrients; nitrogen; phosphorus; runoff; Mediterranean climate; pulses; harmonic analysis; spectral analysis

## 1. Introduction

Nutrient inputs to estuaries have increased as a result of population growth (Peierls et al., 1991; Nixon, 1995), intensification of agriculture (Howarth et al., 1996; Jordan et al., 1997) and changing land use in watersheds (Hopkinson and Vallino, 1995). Application of nitrogen fertilizer worldwide has increased exponentially since the 1940s (Vitousek et al., 1997). Increased fertilizer use and other agricultural practices have resulted in increased nutrient concentrations in rivers, streams, and groundwater (Correll et al., 1995; Jordan et al., 1997; Howarth et al., 2002). Increased nutrient inputs often lead to excessive algal growth and eutrophication, which has resulted in an increase in hypoxia and anoxia in many estuarine and coastal systems (Smith et al., 1992; Rabalais and Turner, 2001).

These high nutrient concentrations often follow precipitation and ensuing runoff events, a linkage that has been observed in estuaries in the United States (Correll et al., 1992;

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Anderson and Taylor, 2001; Verity, 2002), United Kingdom (Balls, 1994) and Australia (Eyre and Twigg, 1997). Nutrient pulses can enhance phytoplankton productivity and water column chlorophyll concentrations in estuaries in as little as hours to as long as weeks following rainfall events (Rudek et al., 1991; Mallin et al., 1993; Hubertz and Cahoon, 1999). However, in some shallow estuaries with short residence times, macroalgae are more effective at intercepting nutrient pulses because phytoplankton tend to wash out of the system via tidal exchange (Valiela et al., 1997).

Our understanding of the effects of nutrient loading to estuarine systems is largely derived from sustained study of large stratified estuaries with relatively long residence times such as Chesapeake Bay, the Baltic Sea, and the Pamlico-Albemarle Sound. In these systems, increased nutrient loading has led to increased phytoplankton production in the surface layer, which then sinks and decomposes in the bottom layer creating hypoxic or anoxic conditions (Smith et al., 1992; Rönnberg and Bonsdorff, 2004). Less is known about how small, well-mixed estuaries with short residence times respond to increased nutrient loading. Specifically how do such systems respond to runoff events and how do physical and biological processes control nutrient concentrations? We conducted an intensive study in Elkhorn Slough, a small estuary located in Central California, to evaluate how runoff events affect nutrient concentrations and the relative importance of biological and physical factors regulating nutrient supply. We examined these dynamics at time scales ranging from long-term changes over two decades to hourly variation at the scale of individual runoff events. We address several specific questions in this study. The decadal time series data allow us to examine whether nutrient concentrations in Elkhorn Slough have changed as land use change and population growth have occurred in the watershed, and to investigate the role of climate variability in controlling runoff. The hourly data allow us to quantify the magnitude and duration of nutrient pulses following specific rain events. We also compare how forcing by other factors, such as tidal mixing and biological uptake, influence nutrient concentrations in Elkhorn Slough. While other studies have examined some of these same questions over short (Caffrey and Day, 1986; Hubertz and Cahoon, 1999; Anderson and Taylor, 2001) and long time scales (Peterson et al., 1985; Verity, 2002), this is the first study to explicitly compare factors controlling nutrient dynamics over multiple time scales (hourly to decadal).

## 2. Methods

### 2.1. Study area

Elkhorn Slough is a small estuary (area 3.25 $km^2$), extending inland for 11.4 km from Monterey Bay in Central California with a watershed area of 182 $km^2$ (Fig. 1). The Slough includes a variety of habitats that experience a range of freshwater/seawater exchanges and nutrient loading. Mean depth in the slough is 2.5 m, with intertidal mudflats and pickleweed marsh (*Salicornia virginica*) bordering the main channel and tidal creeks. Extensive mats of macroalgae (*Ulva* spp., *Enteromorpha* spp. and *Gracilaria* spp.) occur on the intertidal mudflats, while eelgrass (*Zostera marina*) colonizes the shallow subtidal zone near the mouth. Several pocket marshes and shallow ponds are isolated from the main channel by a constructed railbed. These areas have restricted circulation and develop periodic hypoxia and anoxia, while the well-flushed main channel does not. The major freshwater source is Carneros Creek, which has seasonal flow ranging from 0 $m^3 s^{-1}$ in the summer to 3.8 $m^3 s^{-1}$ in the rainy season. Exchange between the upper Slough and Carneros Creek is limited by culverts and flap gates at Hudson's Landing installed in 1995. Azevedo Pond is a small shallow tidal pond (<2 m deep and 4.2 ha) bordered by an 8-ha strawberry farm (Fig. 1). Azevedo Pond is in the upper reaches of the Slough and water exchanges with the main channel through restricted culverts. The South Marsh site is located in a restored salt marsh at the Elkhorn Slough NERR. Exchange between South Marsh and the main channel of the Slough is restricted by the railroad tracks. The Main Channel station is located about 800 m upstream from the mouth of Elkhorn Slough. Water depths in this region are about 6.5 m. Tides in Elkhorn Slough are mixed semi-diurnal with two highs and lows of unequal height (Lower High Water, Higher Low Water, Higher High Water, and Lower Low Water). The mean tidal range along the main channel is 1.7 m. Residence time in the upper

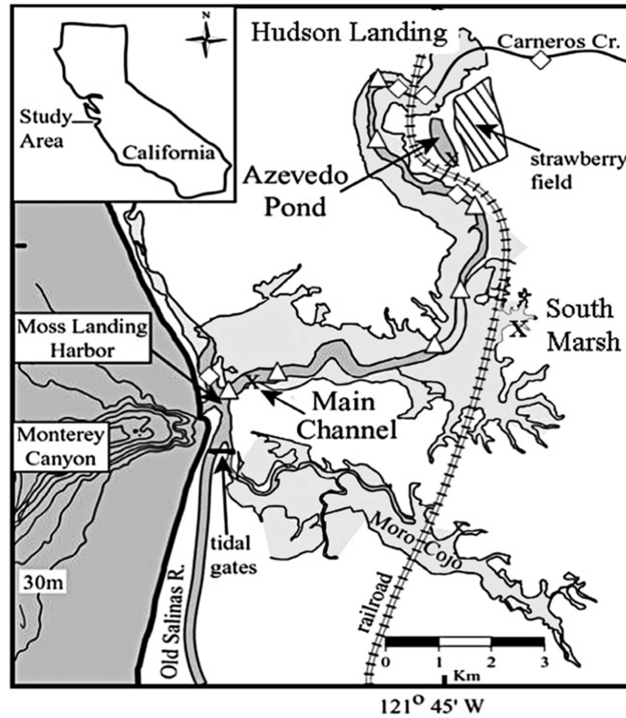


Fig. 1. Map of Elkhorn Slough showing wetland and the main channel. Showing sampling sites from 1974 to 1976 (open triangles), monthly sampling sites along main channel from 1989 to 2000 (open diamonds), data sonde deployment sites at Azevedo Pond, Main Channel and South marsh (X), nutrient analyzers deployed adjacent to data sondes at Azevedo Pond and Main Channel. Monthly samples were also collected between 1989 and 2000 in Azevedo Pond and South Marsh near data sondes.

reaches of the Slough can be 50 days during the dry season (Largier et al., 1997) and about 1 day during the rainy season (Caffrey, unpublished data).

In the 1970s, pastures and dairies were the dominant agricultural land use (Table 1). By the 1990s, many of these lands had been converted to agricultural row crops both along flat areas as well as steep hill slopes next to the Slough (Table 1). Currently, agricultural land use is dominated by row crops such as strawberries, flowers, artichokes, and raspberries, which occur on about 24% of the watershed. Most of the land is zoned rural residential, with a majority of the homes using septic systems. Urban and commercial land uses represent about 16% of the watershed area and are concentrated in the towns of Moss Landing and Castroville. About 14% of the watershed is protected and managed by a variety of state and federal agencies, or private non-profit organizations.

## 2.2. Data sources

### 2.2.1. Monthly data from 1974 to 1976

Water samples from 1 m were collected monthly at seven stations along the Elkhorn Slough main channel (Nybakken et al., 1977) (Fig. 1). Sampling was conducted at high tide between the mouth (km 0.5) and Hudson's Landing (km 10). $NO_3^-$, $NH_4^+$ and DIP were analyzed using standard wet chemical techniques. Salinity was measured using a Beckman induction salinometer.

### 2.2.2. Monthly data from 1989 to 2000

Water samples were collected monthly at seven stations throughout Elkhorn Slough between 1989 and 2000. Five of these stations were located along the estuarine gradient, including Carneros Creek (km 12), Hudson's Landing above the flap gates (km 10.5), Hudson's Landing below the flap gates (km 10), a mid estuary site (km 7.7) and a site at the mouth (km 0.5) (Fig. 1). Two stations (Azevedo Pond and South Marsh) coincide with stations that are part of the National Estuarine Research Reserve (NERR) System Wide Monitoring Program (SWMP). Surface water (0.5 m) was collected without respect to the tide. Water quality parameters (temperature, salinity, dissolved oxygen [DO]) were measured using YSI SCT and DO meters (1989–1995) or using a multiparameter water quality sonde (1995–2000). Between 1989 and 1992, Monterey Bay Aquarium analyzed water samples for $NO_3^-$, $NH_4^+$ and DIP using standard wet chemical techniques. Between 1992 and 2000, Monterey County analyzed nutrients using U.S. Environmental Protection Agency approved methods (APHA, 1985).

Table 1
Land use in Elkhorn Slough Watershed: land cover in hectares

| Land use | 1931[a] | 1981[a] | 1993[b] |
|---|---|---|---|
| Oak woodlands, grasslands and rural residences | 4291 | 3915 | 10522 |
| Pasture | 9848 | 8367 | 162 |
| Total cropland | 2155 | 3781 | 4168 |
| Water bodies | 405 | 405 | 405 |
| Urban, industrial, commercial, highway | 72 | 562 | 2914 |
| Undefined | 1400 | 1141 | 0 |
| Total | 18171 | 18171 | 18171 |

[a] Dickert and Tuttle, 1985.
[b] USDA, 1994.

### 2.2.3. Rainfall data

Annual rainfall data was obtained from National Weather Service station in Watsonville located 6 km away from Elkhorn Slough. Daily rainfall data in Watsonville was obtained from the IPM UC Davis website (http://www.ipm.ucdavis.edu/calludt.cgi/WXSTATIONDATA?MAP=&STN=WTSNVILE.C). Because of California's distinctive climatic patterns, we use the terms rainy and dry to refer to seasonal changes in rainfall and the terms wet and drought to refer to annual changes in rainfall. The data were separated into the rainy season (November–April) and dry season (May–October) and by annual rainfall either into drought years or 'wet' years, which includes both average and above average rainfall years.

### 2.2.4. Hourly data from 1995 to 2001

Hourly data were used to examine diurnal patterns, individual rain events, monthly and seasonal patterns. Temperature, salinity, DO, pH, turbidity and depth were measured using YSI data sondes at the Azevedo Pond and South Marsh SWMP stations between 1995 and 2001. Instrument calibration and data post processing followed NERR protocols (Wenner et al., 2001). In addition, a data sonde was deployed in the Main Channel from April 2001 to November 2001.

The hourly dissolved oxygen data was used to calculate metabolic rates, including net apparent production, gross production, and respiration in Azevedo Pond and South Marsh. The change in oxygen concentrations, accounting for air-sea exchange, during the day is net apparent production, and during the night is respiration. Data summaries and method descriptions for metabolic rate calculations were presented earlier (Wenner et al., 2001; Caffrey, 2003, 2004). A subset of this data was used to examine oxygen changes at slack low water in Azevedo Pond.

We used an in-situ nutrient analyzer, the $NO_3^-$ DigiScan (Monterey Bay Aquarium Research Institute, Moss Landing, CA), to measure $NO_2 + NO_3$ concentrations at hourly intervals. Instrumental and operation details were presented in Chapin et al. (2004). We deployed $NO_3^-$ DigiScans at Azevedo Pond between December 1999 and July 2001 and at the Main Channel site between March 2001 and September 2001. Deployment duration ranged from 1 to 13 weeks with most deployments lasting 5–8 weeks.

## 2.3. Statistical analyses

### 2.3.1. Harmonic regression analysis

Analysis for periodic variance components in the hourly $NO_3^-$ data was performed following Bliss (1970). Harmonic regression analysis has been used extensively for predicting tides and other periodically occurring phenomena. For this analysis we used hourly $NO_3^-$ concentrations measured in Azevedo Pond between December 1999 and July 2001 ($\sim$8700 measurements) and at the Main Channel site between March and July 2001 (~4300 measurements). Periodic components: diurnal (24-h) and $M_2$ tidal (12.4-h), $O_1$ tidal (25.8-h), and $N_2$ tidal (12.66-h), and lunar (29.5-day) were chosen a priori. Because we were most interested in comparing physical and biological forcing, the tidal components, $M_2$ (principal lunar), $O_1$ (principal lunar), and $N_2$ have been grouped together and are referred to in the paper as tidal components. The diurnal signal is a combination of tidal components ($S_2$ [principal solar], $K_1$ [luni-solar], and $K_2$ [luni-solar]) as well as biologically driven processes. The lunar signal responds to forcing by the spring-neap tides as well as irregular events like frontal passage. The $NO_3^-$ concentration data was fit to a linear regression using the formula:

$$NO3_t = a_0 + \sum_{i=1}^{k} a_1 \cos\left(\frac{2\pi \cdot i}{\text{period}} \times t\right) + b_1 \sin\left(\frac{2\pi \cdot i}{\text{period}} \times t\right) \tag{1}$$

where $NO3_t$ is the $\log_{10}$ $NO_3^-$ concentration at time $t$, $a_0$, $a_1$ and $b_1$ are constants, period is the periodic component of interest (e.g., 24-h, 29.5-day), and $k$ is the number of harmonics included. Four harmonics were included for each periodic component. Multiple regression analyses using the log transformed $NO_3^-$ concentrations were conducted for the components for each month. A reduced model removing each of the components was run to estimate the contribution of these components to the total variance. The $NO_3^-$ data has a 2-hour gap every 20 hours when blanks and standards were run instead of samples. Harmonic regression analysis has the advantage over spectral analysis because it does not require interpolation for missing $NO_3^-$ data.

*2.3.2. Spectral analysis*

Unlike harmonic analysis, there are no a priori assumptions about the periods of interest in spectral analysis. We analyzed 14 time series of $NO_3^-$ concentrations from Azevedo Pond and seven from the main channel site. Each series had 512 hourly records, except for the Main Channel September series that had 256 records. Because these time series are only ~21 days in length, we could not examine low frequency phenomena such as frontal passages or spring-neap tidal cycles. Missing data (2-h gaps) were estimated by linear interpolation and were $\log_{10}$ transformed prior to analysis.

*2.3.3. Cross-correlation analysis*

Cross-correlation analysis was used to examine whether two time series were significantly correlated with each other and what sort of time lags there are between the two series. Relationships between DIN or $NO_3^-$ concentrations and metabolic rates were explored using cross-correlation analysis (Shumway and Stoffer, 2000) at daily and monthly time scales. The DIN or $NO_3^-$ concentrations and gross primary production data were log transformed and linear trends were removed. Daily mean $NO_3^-$ concentrations based on $NO_3^-$ DigiScan data were compared to daily gross primary production. Four records from Azevedo Pond with record lengths between 59 and 109 days were used in the cross-correlation analysis. This analysis was also performed on monthly average gross primary production and DIN concentration data from Azevedo Pond and South Marsh between June 1995 and December 2000. The monthly data were log transformed, and linear and seasonal trends were removed before performing cross-correlation analysis.

*2.3.4. Other statistical tests*

Salinity and $NO_3^-$ concentrations at higher high water (HHW) in Azevedo Pond were extracted from the hourly time series. Separate linear regressions of salinity and $NO_3^-$ were performed for rainy and dry seasons. Day and night differences in the hourly change in dissolved oxygen and $NO_3^-$ at slack low water in Azevedo Pond were compared using the non-parametric Kruskal–Wallis ANOVA. This test was used because the data were not normally distributed even after log, square root or arcsine transformations. SYSTAT (Version 9) or ASTSA (Shumway and Stoffer, 2000) were used for all statistical analyses.

## 3. Results

*3.1. Climate*

The 31-year (1970–2000) average annual precipitation at Watsonville was 57.5 ± 4.4 cm, with over 90% of the rain falling between November and April (Fig. 2, top panel). There was a 3-year drought from 1975 to 1977 and a 6-year drought between 1987 and 1992. Peak rainfall occurred in the 1998 water year (119 cm), which was an El Niño year (Fig. 2, bottom panel). Thirteen years had 45 cm of rainfall or less and are defined as drought years in this study (Fig. 2, bottom panel). During these drought years, average rainfall in January and November was about 50% of the long-term average (Fig. 2, top panel). In the wet years, rainfall between November and February was between 20% and 40% higher than the long-term average (Fig. 2, top panel). Rainfall during the 1975 and 1976 water years, for which we have nutrient data, averaged 32 cm/year. In the 1990s, rainfall during the drought years averaged 40 cm/year, while wet years averaged 73 cm/year.

*3.2. Decadal changes in salinity and nutrients*

In order to examine differences between the 1990s and mid 1970s, we compared 1990 drought years with the 1970s data because the 1970s data was collected during a drought. In the mid 1970s, salinity was between 4 and 7 PSU higher than the 1990s in rainy and dry seasons (Fig. 3, top panel). The lower salinity in the 1990s was evident in both the rainy and dry seasons. During the dry season in the 1970s, the upper Slough became hypersaline with salinities exceeding 35, while this was not the case in the 1990s.

The mid 1970s data show peak DIN concentrations (ca. 20 μmol $L^{-1}$) at the 5.5 km station, particularly during the dry season (Fig. 3, middle panel). High $NH_4^+$ concentrations

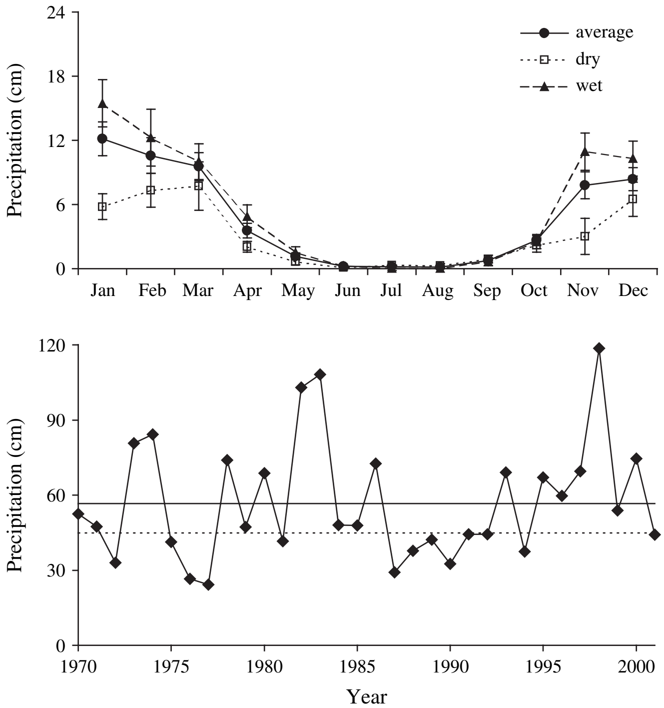


Fig. 2. Precipitation in cm at Watsonville, CA over seasonal (Mean ± S.E., top panel) and interannual periods (bottom panel). Heavy line denotes average annual precipitation and dotted line separates drought years from "wet" years.

(up to 10 μmol $L^{-1}$) in the mid estuary region were responsible for this peak (Nybakken et al., 1977). The 1990s data show high DIN concentrations in the Slough above the 10 km station in both rainy and dry seasons (Fig. 3, middle panel). DIN concentrations at the 10 km station in the 1990s drought years were two times higher than in the 1970s during the rainy season and seven times higher during the dry season. In contrast, concentrations at the 7.7 km station were the same during 1990s and 1970s drought years in both rainy and dry seasons. Although DIN concentrations at the mouth of Elkhorn Slough were lower than the upper Slough in the 1990s, concentrations were often elevated compared with the 7.7 km station, particularly during wet years (Fig. 3, middle panel). DIN concentrations at the mouth during the 1990s doubled compared to the 1970s in the rainy and dry seasons. The increase in the DIN concentrations in the 1990s was due to increased $NO_3^-$ because $NH_4^+$ concentrations in the 1990s and 1970s were similar (data not shown). DIP concentrations during the 1970s did not exhibit a peak at the 5.5 km station as did DIN concentrations. DIP concentrations were similar in the 1970s and 1990s, except at the 10 km station during the dry season where concentrations doubled between the two time periods (Fig. 3, bottom panel).

### 3.3. Seasonal and interannual changes

We examine the effects of climatic variability on salinity and nutrient concentrations by contrasting results from the 1990s wet years and drought years. Salinity values along the main channel were much lower in wet years than drought years, reflecting increased freshwater flow into the Slough (Fig. 3, top panel). This occurred in rainy season, but not during the dry season. Salinity is highest during the dry season when rainfall is at a minimum.

Nutrient concentrations were higher in the wet years compared to drought years at all stations (Fig. 3). Rainy season DIN concentrations at the 10 km station were 109 ± 0.3 μmol $L^{-1}$ and 40 ± 0.3 μmol $L^{-1}$, during wet and drought years, respectively. In addition to the interannual variations associated with wet and drought years, there was a regular seasonal pattern in DIN, with higher concentrations during the rainy season than the dry season. Even during the dry season, DIN concentrations in the upper reaches of the Slough exceeded 40 μmol $L^{-1}$. DIP concentrations were lower near the mouth of the Slough than at the upstream stations (Fig. 3, bottom panel). As with DIN, DIP concentrations were elevated in wet years compared to drought years (Fig. 3, bottom panel). DIP gradually declined along the estuarine gradient (Fig. 3, bottom panel). In contrast to the seasonal pattern of DIN concentrations, dry season DIP concentrations were consistently higher than rainy season values in the upper part of the Slough.

We examined relationships between primary production and DIN concentrations at seasonal and interannual time scales. Primary production was low in the winter (Fig. 4, Caffrey, 2004). In South Marsh, primary production followed a distinct seasonal cycle with a peak between April and July (Fig.4, top panel). Gross production was significantly positively correlated with DIN concentrations with a 1 month lag ($r = 0.47$, $p = 0.05$). Production in Azevedo Pond was much higher than South Marsh and had a distinct seasonal cycle only in 1996 and 1997 (Fig. 4). Production and DIN concentrations were also significantly positively correlated in Azevedo Pond, and there was no lag ($r = 0.75$, $p = 0.05$). The data showed no significant interannual trends such as higher production in the years with higher DIN concentrations.

### 3.4. Daily to seasonal time scales

Time series analyses of high frequency nutrient data when parsed into periods of interest can provide insight into factors controlling nutrient concentrations. For example, the dominance of the purely tidal components over diurnal components would suggest that tidal exchange was more important than diurnal processes such as nutrient uptake by primary producers.

Harmonic regression models for each deployment were all significant ($p < 0.001$). The complete regression model explained from 17% to 93% of the variation in the $NO_3^-$ in Azevedo Pond depending on the time of year (Fig. 5, top panel). The lunar (29.5 days) components dominated during the rainy season and explained as much as 75% of the variation during deployments in January and February 2000 and about 39% of the variation during January and February 2001. Diurnal components (24 h) explained as much as 49% of the variation in $NO_3^-$ and were the dominant component during the spring and summer (April–September 2000 and April–June 2001). In contrast, tidal components (12.4 h) explained a maximum of 30% of the variation and were not as important as the other

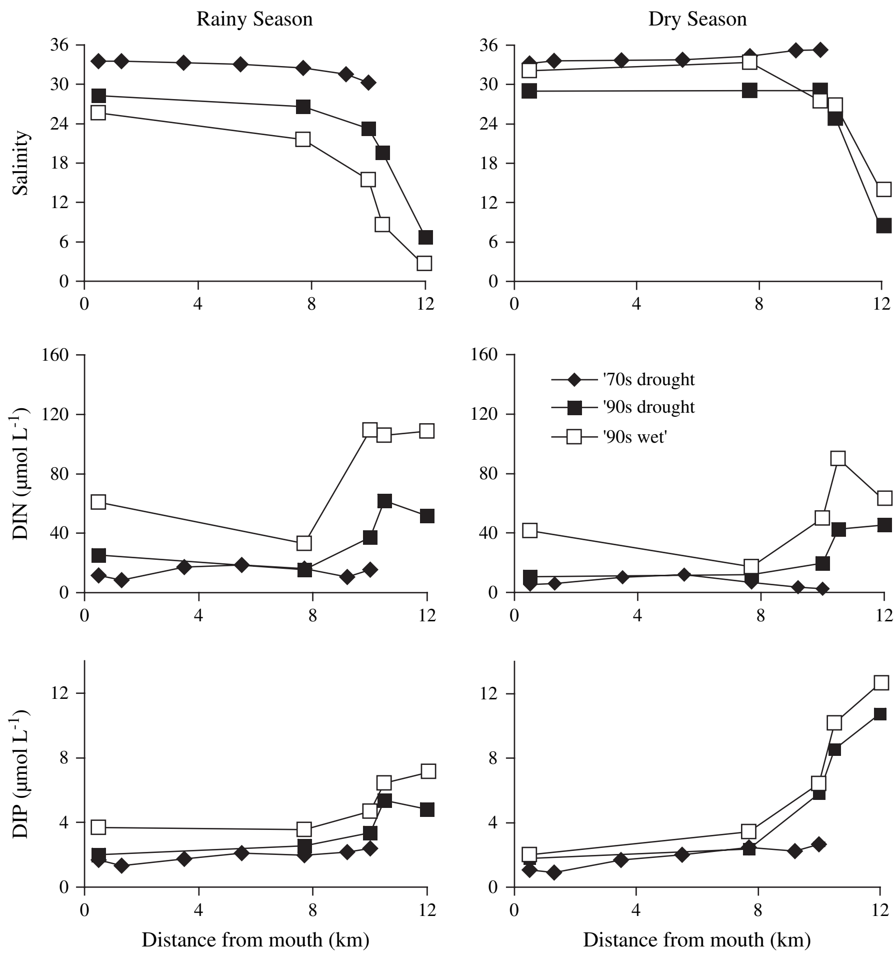


Fig. 3. Salinity (top panel), DIN (middle panel) and DIP (bottom panel) along the Elkhorn Slough main channel. Distances from the mouth in km. Left panels are during the rainy season (Nov.–Apr.) and right panels are during the dry season (May–Oct.). Mean ± S.E. S.E. may be smaller than symbol.

components in explaining variations in $NO_3^-$. The regression models had the poorest fits ($R^2 < 0.23$) in November 2000, December 2000, and July 2001. Visual examination of these time series did not reveal any unusual runoff events or patterns compared to preceding or subsequent time series. The results from spectral analysis were consistent with the harmonic regression analysis. In general, 24-h peaks were greater than the 12.4-h peaks, although there were differences between deployments (data not shown). In March 2000 and 2001, the 12.4-h peak was greater than the 24-h peak in both harmonic regression and spectral analyses. Spectral analysis generated peaks at several periods in addition to the 12.4- and 24-h periods that we thought would be significant. Peaks at other periods in November 2000 (73 h), December 2000 (64 and 85 h), and July 2001 (33 h) may explain why the harmonic regression fits were weak during those months. The peaks in November and December, which are approximately 3-day periods, may have resulted from frontal passages. We do not have any explanation for the 33-h peak in July.

At the Main Channel site, harmonic regression modeling captured between 49% and 85% of the variation in nitrate concentrations (Fig. 5, bottom panel). In contrast to Azevedo Pond, the tidal and lunar components were of similar magnitude and were both greater than the diurnal components. Lunar components explained 23% and 44% of the variation in nitrate concentrations during the rainy season and between 10% and 25% of the variation during the dry season. Tidal components explained as much as 39% of the variation, while diurnal components explained a maximum of 15% of the variation in nitrate concentrations. The regression models were quite similar for all the months. Again, the spectral analysis results were consistent with harmonic regression analysis, although several of the months during the dry season had peaks at 128 and 170 h, again suggesting that longer period phenomena may be important in controlling nitrate concentrations.

### 3.5. High-frequency response to runoff

We examined how individual rain events affected nutrient concentrations. Hourly salinity, water depth, and $NO_3^-$ concentrations were used to contrast the response of Azevedo Pond to two rain events, one during the fall of 2000 at the beginning of the rainy season and the second at the peak of the rainy season in February–March 2001. In October and November 2000, salinity tracked precipitation events in Azevedo Pond. Following rain events, fresh water rapidly mixed with Monterey Bay water throughout the Slough; this water then entered Azevedo Pond on high tides (Fig. 6). However, peak $NO_3^-$

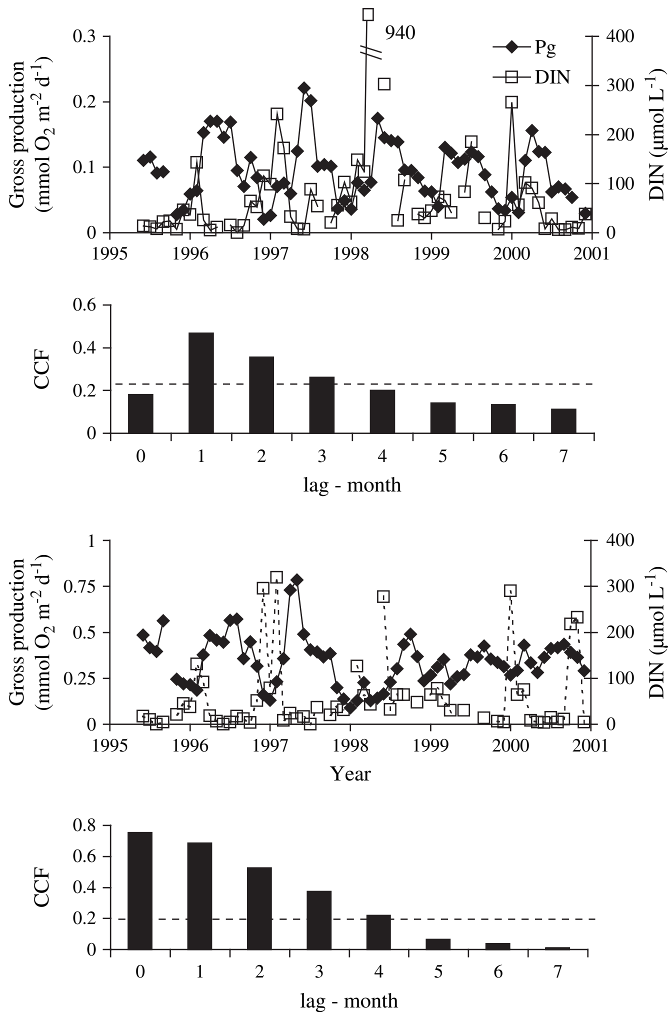


Fig. 4. Gross primary production (Pg) (mmol $O_2$ $m^{-2}$ $d^{-1}$) and DIN concentrations (μmol $L^{-1}$) between May 1995 and December 2000 in South Marsh (top panel), Cross-correlation function (CCF) for primary production and DIN at monthly lag intervals for South Marsh (second from top panel). Azevedo Pond gross primary production (Pg) (mmol $O_2$ $m^{-2}$ $d^{-1}$) and DIN concentrations (μmol $L^{-1}$) between May 1995 and December 2000 (second from bottom panel). Cross-correlation function (CCF) for primary production and DIN at monthly lag intervals for Azevedo Pond (bottom panel). 95% confidence interval shown by dashed line.

concentrations did not coincide with the low salinity. Instead, $NO_3^-$ concentrations lagged the rain events by 3 to 6 days and were between 8 and 19 μmol $L^{-1}$ (Fig. 6). The peaks lasted several hours with low concentrations returning on the following tidal cycles, suggesting that discrete pulses of $NO_3^-$ were moving through the Slough following the fall rains. In contrast, the patterns during the height of the rainy season showed that $NO_3^-$ concentrations in the upper Slough were high throughout this time period. In February and March 2001, high $NO_3^-$ water entered Azevedo Pond on high tides (Fig. 7). Peak concentrations ranged from 40 to 120 μmol $L^{-1}$. $NO_3^-$ concentrations gradually declined and salinity increased over 5–10 days following the March 5 rain event (Fig. 7).

In previous work (Chapin et al., 2004), we illustrated how to separate the sources of high nitrate for Azevedo Pond based on the tide signal. In this analysis, we extract data at higher

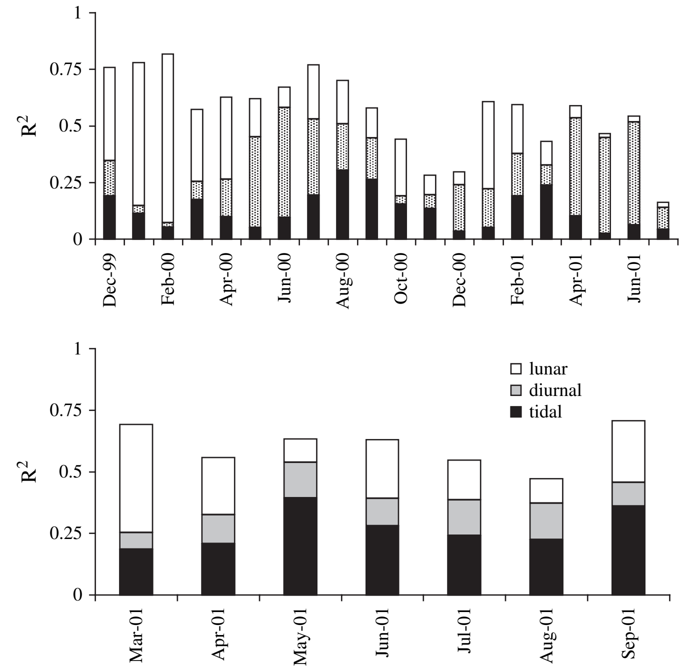


Fig. 5. $R^2$ values obtained from harmonic regression models of log transformed $NO_3^-$ data from Azevedo Pond (top panel) in 2000 and 2001 and Main Channel (bottom panel) in 2001.

high water (HHW) in Azevedo Pond to examine the effect of runoff from Elkhorn Slough on $NO_3^-$ concentrations between January 2000 and July 2001. Approximately 60% of the water volume of the pond was exchanged on higher high

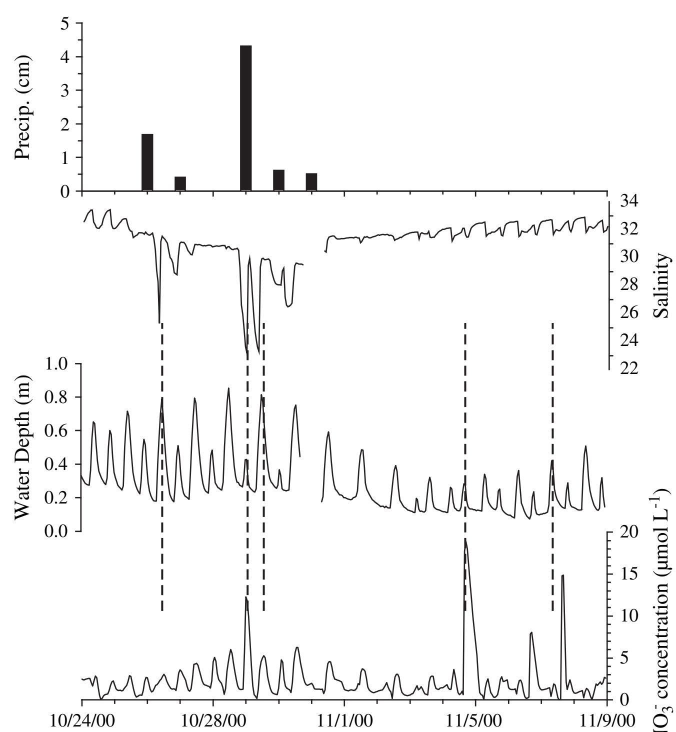


Fig. 6. Daily precipitation (cm), salinity, water depth (m) and $NO_3^-$ concentrations (μmol $L^{-1}$) in Azevedo Pond, 24 October to 9 November, 2000. Dashed vertical lines indicate high tides that coincide with either low salinity or high $NO_3^-$ concentrations.

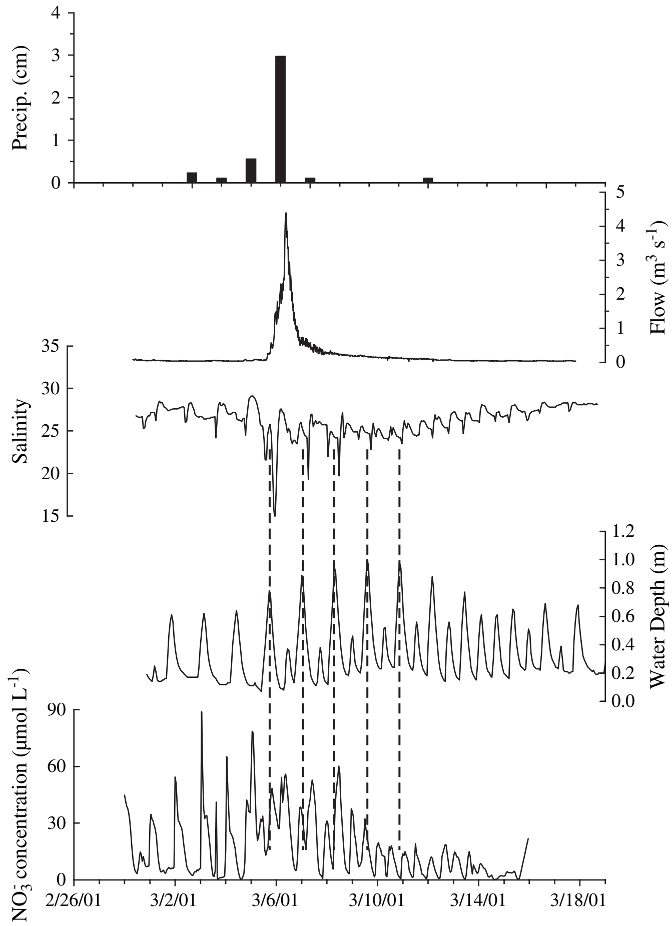


Fig. 7. Daily precipitation (cm), Carneros Creek flow ($m^3$ $s^{-1}$, from Los Huertos et al., 2001), salinity, water depth (m), and $NO_3^-$ concentrations (µmol $L^{-1}$) in Azevedo Pond, 26 February to 18 March, 2001. Dashed vertical lines indicate high tides that coincide with either low salinity or high $NO_3^-$ concentrations.

tides, so the dominant influence on $NO_3^-$ concentrations was water from upper Elkhorn Slough. The salinity response to runoff events was usually immediate while peak $NO_3^-$ concentrations lagged from 1 day to 6 days following rainfall events of 1.5 cm or more. In January 2000, $NO_3^-$ peaks occurred the day after peak rainfall, while in February and March 2000, the lag was about 2–3 days. Similar lags were observed between January and March 2001. In October 2000, the lag was 6 days. The recovery to ‘‘baseline conditions’’ was quite variable when there were multiple rain events. Recovery of salinity and $NO_3^-$ was at the same time scale from 4 to 20 days (Figs. 6 and 7). Low-intensity rainfall events, less than 1.5 cm, had little effect on salinity or $NO_3^-$. Based on these extracted records from Azevedo Pond, salinity and $NO_3^-$ in 2000 and 2001 were significantly negatively correlated during the rainy season ($p < 0.01$, $r = 0.90$), but not during the dry season. Higher rainfall in 2000 led to higher $NO_3^-$ and lower salinity than in 2001.

In order to focus on biological $NO_3^-$ transformations, we examined the change in $NO_3^-$ ($\Delta NO_3^-$) and DO concentrations at slack low water in Azevedo Pond, a period when we expected biological processes to dominate and tidal exchange or advection to be minimal. Net oxygen fluxes were positive during the day, indicating net production (photosynthesis > respiration), and negative at night, indicating respiration (Fig. 8, top panel). Net oxygen flux during the day was significantly different than respiration at night in both seasons ($p < 0.001$) (Fig. 8, top panel). There was no diurnal pattern for $\Delta NO_3^-$ in the rainy season; day and night rates were statistically indistinguishable. In the dry season, $NO_3^-$ uptake during the daylight hours was significantly different than night efflux ($p < 0.001$). The average daytime uptake was $0.52 \pm 0.15$ µmol N $L^{-1}$ $h^{-1}$ while the average night efflux was $0.28 \pm 0.16$ µmol $L^{-1}$ $h^{-1}$ during the dry season. We scaled the daytime oxygen production to nitrogen demand based on a photosynthetic quotient of 1.25 mol $O_2$:mol C and a Redfield ratio of 6.6 mol C:mol N (Valiela, 1984). During the dry season, the $NO_3^-$ uptake was only 20% of the estimated nitrogen demand of primary producers. Thus other nitrogen sources (e.g. $NH_4^+$) must have been required.

Another way of examining the importance of biological processes on $NO_3^-$ concentrations was to compare $NO_3^-$ concentration and gross primary production (calculated using the entire 24-h period). The cross-correlation analysis for two time series, April–May 2000 and February–April 2001, are illustrated. In the raw data series (Fig. 9, top panels), $NO_3^-$ concentrations were high, up to 60 µM at the beginning of the record, and then declined to concentrations between 0 and 10 µM. Gross production ranged between 0.1 and 1.2 mmol $O_2$ $m^{-2}$ $d^{-1}$, with regular peaks in the February–April 2001 time series occurring at 14-day intervals. The periodic components of the data are still apparent in the transformed data (Fig. 9, middle panels). In the April–May 2000 time series, the cross-correlation function (CCF) was significant at the 95% confidence interval at

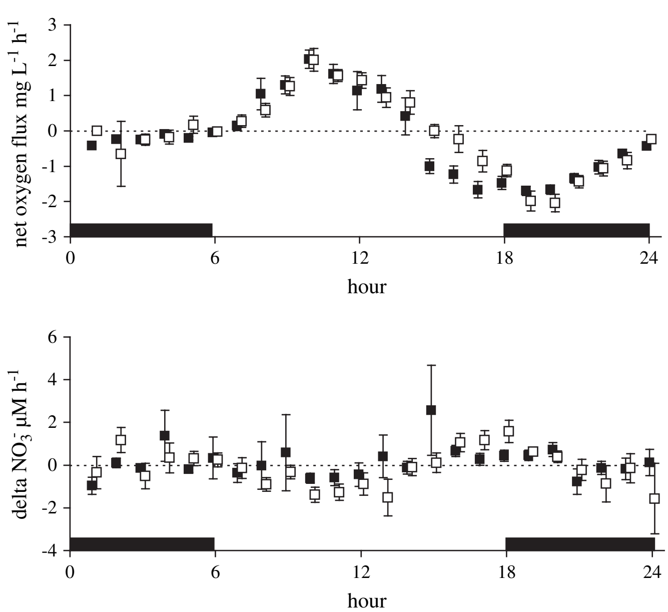


Fig. 8. Hourly changes in dissolved oxygen (µmol $O_2$ $L^{-1}$ $h^{-1}$) (top panel) and $NO_3^-$ concentrations (µmol $L^{-1}$) (bottom panel) in Azevedo Pond at slack low water during rainy (filled) and dry (open) season. Mean and standard error are shown. Black bars indicate night.

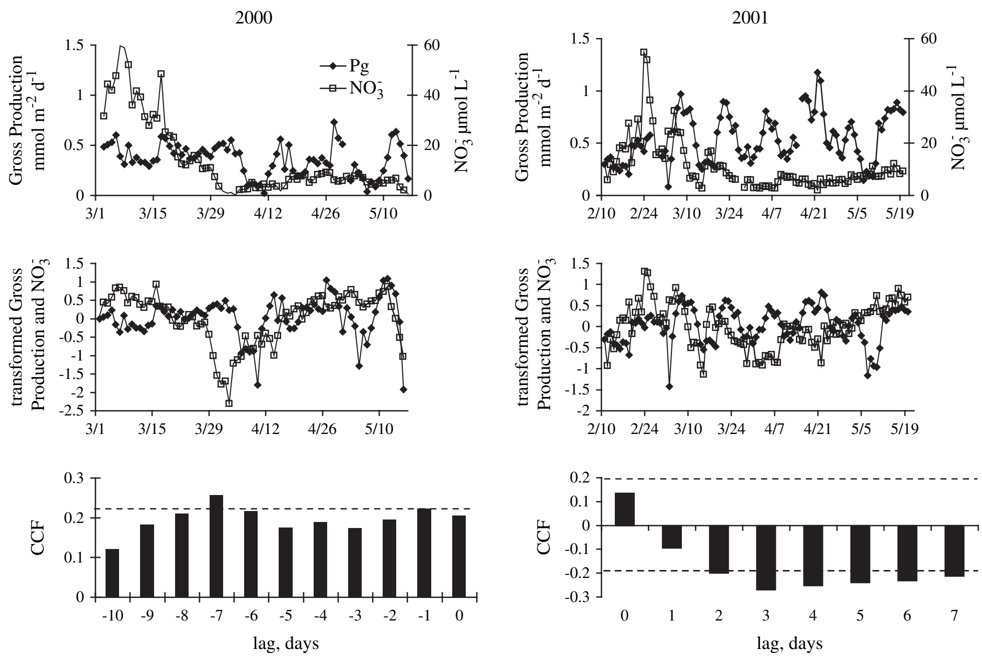


Fig. 9. Mean daily $NO_3^-$ concentrations (μmol $L^{-1}$) and gross primary production (Pg) (mmol $O_2$ $m^{-2}$ $d^{-1}$) April to May 2000 (top left panel) and February to May 2001 (top right panel). Log transformed and linear detrended $NO_3^-$ concentrations and gross primary production (middle panels). Cross-correlation function (CCF) at different daily lags (bottom panels). 95% confidence interval shown by dashed line.

−7 days with a positive relationship between $NO_3^-$ and primary production (Fig. 9, bottom left). This means that the $NO_3^-$ and primary production were significantly positively correlated and that primary production increased 7 days following $NO_3^-$ pulses. In the February−April 2001 time series, $NO_3^-$ and primary production were negatively correlated and the CCF was significant at +2 to +8 days, although the +3 day lag had the strongest correlation (Fig. 9, bottom right). This indicates that increased removal of $NO_3^-$ occurred 3 days after periods of high production. In June−July 2001, $NO_3^-$ and primary production were positively correlated with no lag (data not shown). No relationship between primary production and $NO_3^-$ concentrations were observed for the October 2000−January 2001 time series.

## 4. Discussion

Five processes critical in controlling DIN concentrations in Elkhorn Slough are runoff, uptake, remineralization, denitrification and tidal exchange (Fig. 10). This discussion focuses on how runoff, uptake and tidal exchange control DIN concentrations as remineralization and denitrification have been discussed in previous studies (Caffrey, 2002; Caffrey et al., 2002a, 2003). High nutrient, fresh water runoff affects $NO_3^-$ concentrations over the widest range of time scales from hourly to decadal, while tidal exchange mainly operates over hourly to fortnightly time scales.

### *4.1. Long-term changes in Elkhorn Slough*

Climate, as it affects freshwater runoff, can be the dominant factor controlling salinity in West Coast estuaries, such as San Francisco Bay (Peterson et al., 1989). Our study of Elkhorn Slough showed significant declines in salinity along the main channel between the 1970s and 1990s. Climatic variability is clearly important in Elkhorn Slough, with higher salinity during periods of drought and low salinity during years with high precipitation (Fig. 11, top panel). In contrast to the relationship between salinity and precipitation, there was no correlation between DIN concentrations and precipitation at the 10 km station (Fig. 11, middle panel). In fact, DIN concentrations were often highest during years with intermediate rainfall values. Although there is a relationship between salinity and DIN (Fig. 11, bottom panel), it explains less than half of the variability in DIN concentrations.

Other factors also contribute to the interannual salinity variability including increased use of groundwater for agriculture, agricultural conversion from pastures to row crops that use plastic for weed control and thus increase runoff, farming

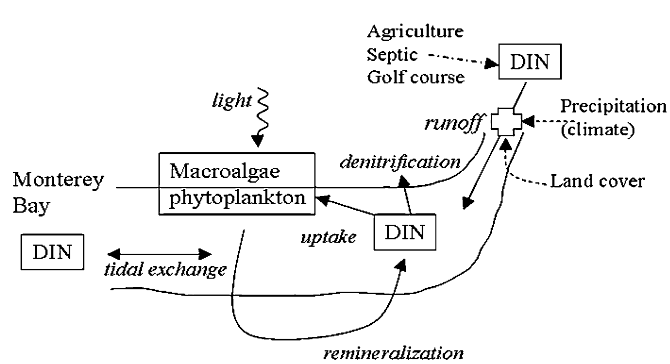


Fig. 10. Conceptual model highlighting the dominant factors controlling DIN concentrations in Elkhorn Slough.

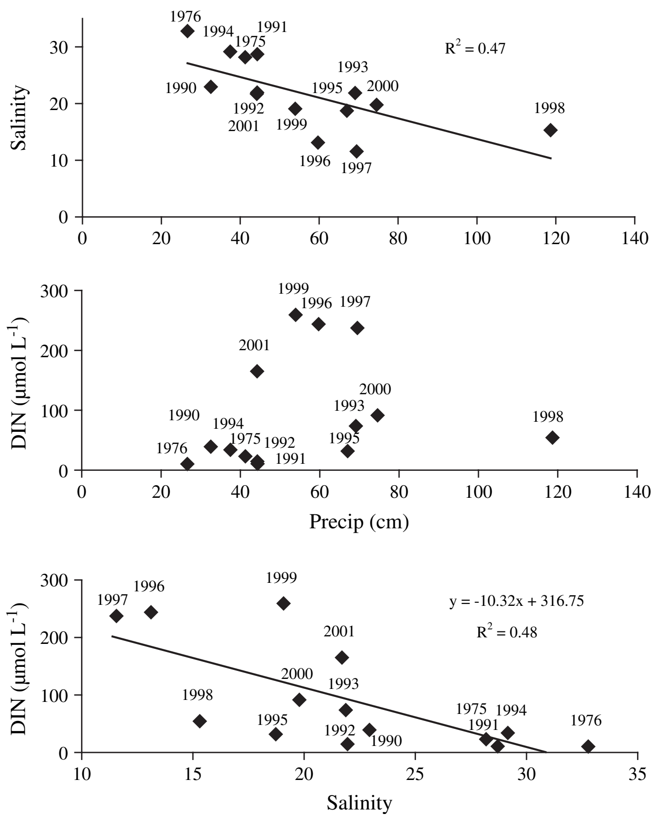


Fig. 11. Average rainy season salinity versus annual precipitation (cm) (top panel), average rainy season DIN (μmol $L^{-1}$) versus annual precipitation (cm) (middle panel), average rainy season DIN (μmol $L^{-1}$) versus average rainy season salinity (bottom panel) from the 10 km station in 1975–1976 and 1990–2001.

adjacent to the Slough without buffer strips, farming on steep slopes, and increased population (Caffrey et al., 2002b). Population growth generates more freshwater runoff due to the increased amount of impervious surfaces and increased inputs from septic systems (Dickert and Tuttle, 1985). Similar changes in salinity associated with land use changes have been observed in the Patuxent Estuary following deforestation (Cronin and Vann, 2003).

Changing farming practices and population increases may be responsible for the doubling of DIN concentrations observed at the 10 km station and at the mouth between the 1970s and 1990s. During this period, pastures and steep hill slopes were converted to row crops such as strawberries that require extensive fertilization (Table 1). Similar responses to intensification of agriculture and population growth been observed in Chesapeake Bay tributaries (Jordan et al., 1997), several North Carolina estuaries (Mallin, 1994, 2000), Skidaway River estuary (Verity, 2002) and Scottish estuaries (Balls, 1994; Balls et al., 1997). Plots comparing the two time periods suggest that there were different nutrient sources to the Slough in those decades (Fig. 3). Mid estuary DIN peaks (primarily $NH_4^+$) in the 1970s were attributed to runoff from dairy farms in this region (Nybakken et al., 1977). Peaks in DIN and DIP from the 1990s data appeared in the upper part of the Slough, suggesting that runoff from various sources, including row crops, a golf course and septic tanks, is significant in this region.

### 4.2. Factors operating at interannual and seasonal time scales

We observed significant interannual variations in nutrient concentrations and salinity, with wet years having much higher nutrient concentrations than drought years. In contrast, there were no significant interannual variations in gross primary production, probably because rainfall and nutrient supply are not the only factors controlling production. The seasonal pattern of rainfall resulted in distinct differences in nutrient concentrations and salinity between the seasons, with the highest nutrient occurring during the rainy season. Higher rainy season DIN concentrations at the mouth than the mid estuary station were likely due to high nutrient inputs from agricultural drainage ditches into the old Salinas River channel, which drains into Moss Landing harbor near the mouth of the Slough (Caffrey, 2002; Fry et al., 2003; Chapin et al., 2004). Thus, there were nitrogen inputs from both the upper reaches of the Slough and near the mouth.

Both harmonic regression and spectral analyses showed consistent differences between wet and dry season, with greater variability explained by tidal and diurnal signals in the dry season. Based on the harmonic regression analyses, between 7% and 60% of $NO_3^-$ variability could be explained by tidal or diurnal signal, while the remaining variability is most likely driven by runoff. The good agreement between harmonic regression and spectral analyses indicates that our selection of periods in the harmonic regression analysis captured most of the variation in the data. In contrast, an analysis of hourly salinity records from Azevedo Pond and South Marsh found that tidal and diurnal signals explained between 50% and 99% of the variability in the salinity signal (D. Edwards, personal communication).

Although physical forcing had a greater effect on $NO_3^-$ concentrations than biological forcing, biological processes were significant during the dry season in Elkhorn Slough. Both time series analyses showed enhancement of the diurnal signals during the dry season compared to the rainy season. In addition, $NO_3^-$ uptake in Azevedo Pond during the day at low slack water occurred during the dry season, but not during the rainy season (Fig. 8, bottom panel). This is not surprising because the rainy season is a period when temperatures are low, day length is short, and production is at a minimum. $NO_3^-$ uptake during the dry season could supply a small, but significant percentage (20%) of the nitrogen demand by primary producers.

Similar seasonal and interannual patterns in nutrient concentrations have been observed in San Francisco Bay and Tomales Bay. Spring snowmelt in the Sierra Nevada mountains lead to nearly conservative distribution of inorganic nutrients in North San Francisco Bay (Peterson et al., 1985). In contrast, during the summer low flow periods, nutrient distributions were significantly affected by phytoplankton uptake in both North San Francisco Bay and Tomales Bay (Peterson et al., 1985). Interannual variations in river flow and upwelling intensity affected nutrient salinity relationships (Peterson et al., 1985). Tomales Bay is similar to Elkhorn Slough in that freshwater and nutrient runoff occurs during the rainy season, the period when nutrient concentrations are highest (Smith and Hollibaugh, 1997). Upwelled $NO_3^-$ represents a significant nutrient source to Tomales Bay and controls ecosystem metabolism in this system (Smith and Hollibaugh, 1997). We also observed the upwelling signal in our $NO_3^-$ time series at the mouth of Elkhorn Slough (Chapin et al., 2004).

### 4.3. Slough response to pulses and tidal exchange

$NO_3^-$ runoff to Elkhorn Slough appears to be coming in with baseflow or groundwater that is diluted during rainfall events (Los Huertos et al., 2001). Coincident measurements of $NO_3^-$ concentrations in upper Carneros Creek (Los Huertos et al., 2001) and Azevedo Pond showed a 10-fold reduction in concentrations over 7.5 km as the water traveled from the upper reaches of Carneros creek to the inlet of Azevedo Pond. This is likely due to dilution with low $NO_3^-$ water in the upper Slough although uptake and denitrification in riparian zones and marshes at the head of the Slough may also have contributed. This high nutrient, freshwater runoff enters Elkhorn Slough after storms with rainfall greater than 1.5 cm. Freshwater pulses lead to brief periods of lower salinity early in the rainy season or extended freshets later in the rainy season. The duration and magnitude of these nutrient pulses depends on whether they occur early in the rainy season when they are rapidly flushed out of the system (Fig. 6) or later in the rainy season when they can persist for weeks (Fig. 7). The rapid flushing of pulses out of the Slough occurs because of the combination of tidal range and morphometry of the Slough. The high tide volume is three times higher than the low tide volume and the tidal excursion is 5.7 km. This leads to rapid mixing of water from the mid and lower reaches of the Slough with water from Monterey Bay. Similar pulses of freshwater runoff with high nutrient concentrations have been observed in North Carolina estuaries (Mallin et al., 1993; Hubertz and Cahoon, 1999), the Ythan estuary (Balls et al., 1997) and the Richmond River estuary (Eyre and Twigg, 1997).

### 4.4. Response by primary producers to nutrient variability

A number of estuaries have shown increased phytoplankton biomass in response to increased nutrient loading (Smith et al., 1992; Mallin et al., 1993; Hubertz and Cahoon, 1999; Anderson and Taylor, 2001). However, macrotidal estuaries (tide range $> 2$ m) show a lower response of phytoplankton biomass to DIN concentrations than microtidal (tide range $< 2$ m) systems (Monbet, 1992). Macroalgal biomass can also be enhanced at the expense of phytoplankton in estuaries with short residence times since macroalgae are less likely to be washed out of the estuary (Valiela et al., 1997). Decoupling of nutrient uptake and primary production can occur in macroalgae dominated systems (Pedersen and Borum, 1997; Kamer et al., 2001; Fong et al., 2004).

Elkhorn Slough is a very productive estuary; water column chlorophyll concentrations can exceed 100 $\mu g\ L^{-1}$ at the head of the Slough and in areas with restricted circulation (Caffrey et al., 2002a), as well as extensive mats of macroalgae, intertidal marshes and benthic microalgae. Although historical chlorophyll data from Elkhorn Slough is limited, chlorophyll *a* concentrations in the middle reaches and the mouth were unchanged between the 1970s and 1990s, about 3.4 $\mu g\ L^{-1}$ with a range of 0.3–13.3 $\mu g\ L^{-1}$ (Zimmerman and Caffrey, 2002; Caffrey et al., 2002a, Caffrey, unpublished data). Tidal exchange and short residence time may rapidly dilute phytoplankton biomass as well as nutrients in the lower reaches of the Slough. Seasonality or interannual trends in macroalgal production and biomass in the Slough have not been studied. Thus, there is insufficient data to determine whether the decadal scale changes in nutrient concentrations have led to concomitant changes in the biomass or composition of Slough primary producers.

However, estimates of primary productivity in the Slough from 1995 on suggest that productivity was often enhanced following nutrient pulses. The South Marsh site had a 1-month lag in productivity following high DIN concentrations, while the Azevedo Pond site responded more rapidly with no lag in productivity following high DIN. In the daily data analyzed from Azevedo Pond, $NO_3^-$ concentrations and productivity were significantly correlated for three of the four time series and lag times ranged from 0 to 7 days, consistent with the monthly analysis showing no lags.

Primary production may be limited by factors other than $NO_3^-$ concentrations, such as variability in solar radiation, water column light attenuation, and other nutrient concentrations such as $NH_4^+$ and DIP (Valiela, 1984; Cloern, 1999). Beck and Bruland (2000) observed nutrient uptake of $NH_4^+$ and DIP during warm summer days in Azevedo Pond and release at night when the pond went anoxic. The light field is highly variable both spatially (Nybakken et al., 1977) and temporally (Zimmerman et al., 1994). Light attenuation ($k$) ranged from 2.7 $m^{-1}$ in the upper Slough to 0.8 $m^{-1}$ at the mouth (based on $k = 1.7$/secchi disk depth, Nybakken et al., 1977; Parsons et al., 1977). Zimmerman et al. (1994) did not observe any seasonal pattern in light attenuation. Values varied from 1 to 6 $m^{-1}$ over period of several days (Zimmerman et al., 1994). These generally high attenuation coefficients are consistent with light limitation of phytoplankton production. Second, ambient nutrient concentrations at or below nutrient half saturation constants ($K_s$) have been used as an indicator of nutrient limitation (Valiela, 1984; Cloern, 1999). $NO_3^-$ concentrations in the main channel of Elkhorn Slough during the summer are almost always higher than $K_s$ values for most phytoplankton species while concentrations in Azevedo Pond are regularly below $K_s$ values (Fig. 3, Chapin et al., 2004). Thus, the enhanced primary production following $NO_3^-$ pulses that we observed in Azevedo Pond may not occur in the main channel of the Slough where turbidity and tidal flushing is greater.

## 5. Conclusions

We have used a variety of techniques to examine how variability in DIN concentrations can be attributed to physical processes such as runoff and tidal exchange as well as biological uptake. In Elkhorn Slough, increased DIN concentrations in the upper Slough over a two decades occurred as agricultural practices intensified and as population increased. Elkhorn Slough, with its Mediterranean climate and distinct seasonal runoff, has some similarities to Atlantic estuaries in the watershed response to changing agricultural practices and precipitation events. During the winter rainy season, rainfall events led to pulses of high nutrient concentrations in the Slough, a pattern observed in other estuaries. Uptake of nitrate by primary producers was significant during the dry season, but not the rainy season. While primary production was enhanced by nutrient pulses, chlorophyll *a* concentrations were not. Thus, the biological response to nutrient inputs in Elkhorn Slough appears more muted than in larger estuaries with longer residence times (Hopkinson and Vallino, 1995; Howarth et al., 1996).

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