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Nitrate Sources and Sinks in Elkhorn Slough, California: Results from Long-term Continuous in situ Nitrate Analyzers

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ABSTRACT: Nitrate and water quality parameters (temperature, salinity, dissolved oxygen, turbidity, and depth) were measured continuously with in situ NO_3 analyzers and water quality sondes at two sites in Elkhorn Slough in Central California. The Main Channel site near the mouth of Elkhorn Slough was sampled from February to September 2001. Azevedo Pond, a shallow tidal pond bordering agricultural fields further inland, was sampled from December 1999 to July 2001. Nitrate concentrations were recorded hourly while salinity, temperature, depth, oxygen, and turbidity were recorded every 30 min. Nitrate concentrations at the Main Channel site ranged from 5 to 65 μM. The propagation of an internal wave carrying water from ~100 m depth up the Monterey Submarine Canyon and into the lower section of Elkhorn Slough on every rising tide was a major source of nitrate, accounting for 80–90% of the nitrogen load during the dry summer period. Nitrate concentrations in Azevedo Pond ranged from 0–20 μM during the dry summer months. Nitrate in Azevedo Pond increased to over 450 μM during a heavy winter precipitation event, and interannual variability driven by differences in precipitation was observed. At both sites, tidal cycling was the dominant forcing, often changing nitrate concentrations by 5-fold or more within a few hours. Water volume flux estimates were combined with observed nitrate concentrations to obtain nitrate fluxes. Nitrate flux calculations indicated a loss of 4 mmol NO_3 m^{-2} d^{-1} for the entire Elkhorn Slough and 1 mmol NO_3 m^{-2} d^{-1} at Azevedo Pond. These results suggested that the waters of Elkhorn Slough were not a major source of nitrate to Monterey Bay but actually a nitrate sink during the dry season. The limited winter data at the Main Channel site suggest that nitrate was exported from Elkhorn Slough during the wet season. Export of ammonium or dissolved organic nitrogen, which we did not monitor, may balance some or all of the NO_3 flux.

Introduction

Inputs of nutrients to estuaries, especially nitrogen and phosphorus, have grown with increasing population and intensification of agricultural practices (Vitousek et al. 1997). Elevated nutrient loads are associated with declines in water quality in many estuaries and have been implicated in the occurrence of eutrophication, nuisance and harmful algal blooms, and hypoxic events (Nixon 1995; Nixon et al. 1995; Rabalais et al. 1996; NRC 2000). These concerns prompted the development of systematic monitoring programs by citizen groups and state and federal agencies to determine nutrient loads to estuaries and evaluate long-term trends and success in nutrient reduction programs (NRC 2000).

Most nutrient monitoring programs are conducted at monthly, or at best, weekly intervals. While monthly monitoring of nutrients can usually determine the overall seasonal nutrient distribution, it is widely recognized that low temporal resolution sampling can miss important details of transient events such as diel cycling, the effects of tidal forcing, episodic weather events, and algal blooms (Caffrey and Day 1986; Boynton et al. 1995; Hubertz and Cahoon 1999; Glasgow and Burkholder 2000). Monitoring these transient events, which may contribute the bulk of the annual nutrient loading, is essential for an accurate assessment of nutrient fluxes. Nutrient concentrations and physical conditions in estuaries should be monitored with a temporal resolution of 1 h to adequately resolve events such as tides, diel cycling, and episodic runoff events. Hourly sampling will also enable a better understanding of the biological processes associated with nutrient cycling.

While the need for long-term continuous in situ monitoring of nutrients is clear, the realization of instrumentation for such tasks has proven to be a

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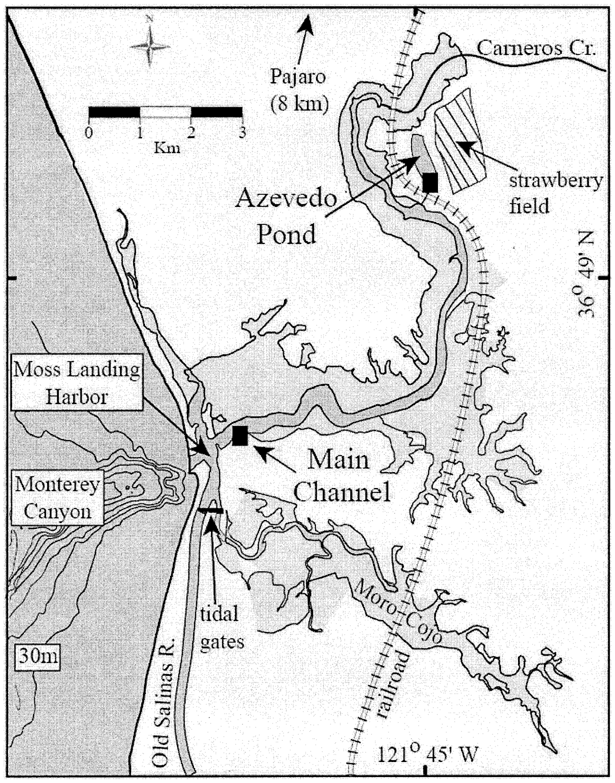

Fig. 1. Map of Azevedo Pond and Main Channel study sites in Elkhorn Slough in Monterey Bay, CA. Dark gray indicates water level at low tide, light gray indicates water level at high tide. The NO_3-DigiScan and YSI Sonde in situ instruments were located at positions marked with a black square.

difficult challenge (Varney 2000). MBARI (Monterey Bay Aquarium Research Institute) recently developed an in situ nitrate analyzer, the NO_3-DigiScan (NO_3-Digital Submersible Chemical Analyzer), which has provided continuous autonomous nitrate measurements for over 90 d with hourly sampling. The NO_3-DigiScan can accurately monitor nitrate variations within the rapidly changing salinity, temperature, and turbidity conditions found in estuaries. We examine how short-term and long-term changes in nitrate concentrations reflect tidal cycling, biological processes, and runoff from agricultural fields in Elkhorn Slough, an estuary in Monterey Bay, California.

Materials and Methods

STUDY AREA

Elkhorn Slough is a shallow estuary (mean depth 2.5 m) that extends inland 11 km from Monterey Bay in Central California (Fig. 1). Waters of Elkhorn Slough lie within the Monterey Bay National Marine Sanctuary and portions of the surrounding marsh form the Elkhorn Slough National Estuarine Research Reserve. Elkhorn Slough has a surface area of 9.1 km^2 and drains a watershed of 585 km^2 (Malzone 1999). Agricultural land use with extensive application of fertilizer occurs year round on about 26% of the watershed. Large agricultural areas diked since the early 1900s were breached in the 1980s to reclaim wetland areas and these new shallow wetlands comprise 4.3 km^2 (48%) of the total Elkhorn Slough area (Malzone 1999; Caffrey and Broenkow 2002). Elkhorn Slough connects to Monterey Bay via the Moss Landing Harbor, which was created and dredged in 1947. The Monterey Submarine Canyon begins just offshore from the entrance to Elkhorn Slough and provides a conduit for deep-sea waters to reach Elkhorn Slough (Fig. 1).

Elkhorn Slough is a seasonal estuary. The only significant surface water inputs occur sporadically during the winter rainy period via Carneros Creek, an ephemeral stream (Fig. 1; Los Huertos et al. 2001; Caffrey and Broenkow 2002). Elkhorn Slough has mixed semidiurnal tides with an estimated tidal prism of 5.7×10^6 m^3 from mean high high water to mean low low water, while total slough volume is 5.5×10^6 m^3 at mean low low water (Wong 1989; Malzone 1999). The main transport mechanism for water is tidal exchange. Monterey Bay seawater reaches 5–6 km inland at high tide and 50–75% of the entire slough volume is typically flushed with each tidal cycle (Wong 1989; Malzone 1999).

Moro Cojo Slough and the Old Salinas River channel drain intensively farmed lands to the south of Elkhorn Slough and enter the southern end of Moss Landing Harbor through tidal gates (Fig. 1; Caffrey 2002). These relatively warm, high nitrate waters pass through the tidal gates during the falling tide and result in elevated nitrate concentrations in the southern end of Moss Landing Harbor.

We deployed in situ NO_3 analyzers and water quality sondes at two sites within Elkhorn Slough (Fig. 1). The Main Channel deployment site was located on an abandoned power plant outfall situated 800 m from the mouth of Elkhorn Slough. Instruments were deployed at the end of a concrete wall that extends 5 m from the shoreline into the main channel of Elkhorn Slough. Instruments were protected by placement in vertical PVC tubes that extended to the bottom and were perforated below the waterline. Instruments were submerged within the tubes to a fixed depth 1 m above the bottom and 2 m below the surface.

The channel width at the Main Channel site is 150 m and the maximum depth is 6.5 m (Malzone 1999). The tidal range in this part of Elkhorn Slough is 2 m and the tidal currents may exceed 1.5 m s^{-1} (Malzone 1999). Previous work has demonstrated that the water flowing past the Main Channel site is well mixed vertically (Wong 1989; Malzone 1999). We assume that the NO_3-DigiScan and YSI Sonde in the Main Channel record the average properties of all the water flooding into and ebbing out of the main body of Elkhorn Slough. Except during winter precipitation periods, Elkhorn Slough does not receive any significant surface water inputs, so we can approximate Elkhorn Slough as one reservoir with an inlet and outlet through the Main Channel site.

The upper Elkhorn Slough study site, Azevedo Pond, is a small shallow tidal pond (< 1.5 m deep and 4.2 ha) bordered by an active 8 ha strawberry farm (Fig. 1). Azevedo Pond is further inland than the tidal prism, so waters entering Azevedo Pond have remained in the Upper Elkhorn Slough area for several tidal cycles. Azevedo Pond only receives groundwater and surface runoff input from the surrounding strawberry farm during rain events. The pond has thick algal mats of *Enteromorpha* sp. and *Ulva* sp. during the summer and fall months (Caffrey 2002).

Azevedo Pond is slightly elevated above Elkhorn Slough and is connected to Elkhorn Slough by an open culvert that runs under the Southern Pacific Railroad bed (Fig. 1). Water exchange between Azevedo Pond and Elkhorn Slough is partially restricted by the elevated culvert and Azevedo Pond is only flushed with Upper Elkhorn Slough water when the tide height is greater than 1.2 m. During neap tide periods, Azevedo Pond is only flushed once per day. The lack of tidal flushing results in long quiescent periods and a thermal stratification can develop on sunny days (Beck and Bruland 2000). The restricted water flow, shallow depth, and high productivity of Azevedo Pond result in large diel changes in temperature and oxygen during the summer and fall (Beck and Bruland 2000; Beck et al. 2001).

The instruments in Azevedo Pond were located just inside the entrance of the culvert to sample the inflow and outflow of water from the pond. The inlet of the NO_3-DigiScan was placed next to the sampling probe of the sonde, approximately 10 cm above the sediments to insure that the sample inlet was submerged during the lowest tides (20 cm depth). The instruments observed mainstem Upper Elkhorn Slough water during the flood tide. The incoming waters then mixed with waters remaining in the middle and upper reaches of Azevedo Pond. With the ebbing tide, the mixed water drained from Azevedo Pond and the instruments recorded its properties.

SAMPLING AND PROCEDURES

Nitrate concentrations were determined with the NO_3-DigiScan developed at the MBARI (Weeks and Johnson 1996). An overview description of the instrument is presented here. The NO_3-DigiScan instrument measured nitrate + nitrite with the standard nitrate colorimetric method using cadmium (Cd) reduction and azo dye formation (Brewer and Riley 1965). The NO_3-DigiScan consists of 3 components: a watertight housing containing the controller, data logger, and battery; an oil-filled pressure compensated housing containing the solenoid driven diaphragm pumps and detector; and reagents bags and flow manifold (Fig. 2). Solenoid pumps propelled sample (or standards) and buffer through the Cd column. Sulfanilamide and N-1-napthylethylene-diamine (NED) were then added to produce the colored reaction complex with an adsorption maximum at 540 nm. These solutions flowed through a mixing coil and into the flow cell. The flow cell contains a photo detector and a light emitting diode (LED) with a peak emission at 565 nm and a 30 nm spectral line halfwidth. Measuring light transmission on the shoulder of the adsorption peak and using a relatively broad emission source resulted in less sensitivity but greater linear range when compared to a laboratory spectrometer. After the transmission reading was taken, a cleaning solution was passed through the detector and the NO_3-DigiScan was thoroughly flushed with sample water before the next analysis. The sample inlet was a 10 μm high-density polyethylene solvent filter (Upchurch A-426).

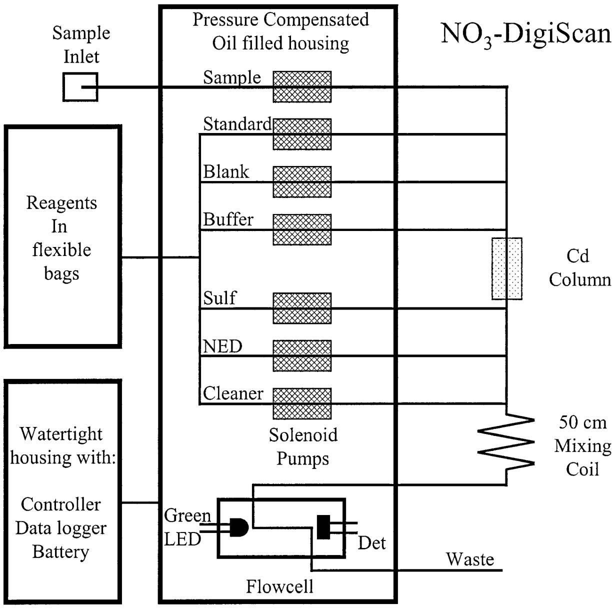

Fig. 2. NO_3-DigiScan flow schematic. Solenoid pumps are indicated by hatched rectangles. The data logger controls the operation of all the pumps and the detector and stores the data.

The nitrate calibration curve was linear up to

100 µM. Values above 100 µM were estimated by fitting standards to a quadratic standard curve. Deployment duration ranged from 7 to 90 d with most deployments lasting 5–8 wk. More than 9,900 samples were analyzed in situ at Azevedo Pond from December 1999 to July 2001, while more than 4,700 in situ samples were analyzed at the Main Channel site from March to September 2001. The stability of the NO_3-DigiScan over the course of the deployment was evaluated by running nitrate standards and blanks every 20 h. Base line shifts due to dye coating in the detector ranged from 5% to 40% depending on the length of deployment. Cd column reduction efficiencies at the beginning of deployments were 90–100%. Cd reduction column efficiencies at the end of deployment usually ranged from 80% to 90% but dropped as low as 70% in a few deployments. The effects of a detector base line shift or a decrease in the Cd column reduction efficiency were corrected with standardization every 20 h. Unfiltered discrete samples for intercomparison with NO_3-DigiScan results were hand collected 1–2 times per week and frozen for later analysis on an Alpkem rapid flow analyzer according to procedures developed at MBARI (Sakamoto et al. 1990).

The large changes in ambient temperature, salinity, and particle load that are often found in estuaries can be very problematic for colorimetric nitrate analysis. Temperature effects on the reaction chemistry were minimized by allowing the color development of the reaction product to proceed for 55 min before the light transmission reading was recorded. Thermal effects on the detector were also corrected with a temperature compensation equation. Salinity effects on the nitrate chemistry and refractive index changes can cause problems in the standard nitrate analysis. The NO_3-DigiScan used a much higher reagent to sample ratio than the standard chemistry, 3 parts reagent to 1 part sample, so changes in sample salinity have little effect on the overall refractive index and nitrate chemistry. The 10 µm filter on the inlet of the NO_3-DigiScan provided coarse filtering at the sample inlet while the Cd reduction column acted as a fine filter. Fine particles trapped at the head of the Cd column preventing their passage to the detector and turbidity effects in the detector were not observed.

Additional chemical and physical data at the Azevedo Pond and the Main Channel site were collected with YSI Sonde 6000 multiparameter water quality monitors as part of the National Estuarine Research Reserve (NERR), System Wide Monitoring Program. These instruments determined temperature, conductivity (converted to practical salinity units, psu), depth, pH, dissolved oxygen, and turbidity at 30-min intervals. The YSI Sondes were deployed for a 30-d period. After 30 d, the sonde was recovered and a new freshly calibrated sonde was immediately deployed to minimize gaps in data collection. Instrument calibration was performed as outlined in the YSI manual. The pH, conductivity, and turbidity sensors were calibrated with standard solutions (pH 7 and 10 buffers, 53 mS cm^{-1} conductivity standard, and 0 and 100 NTU turbidity standards). New oxygen membranes were attached and allowed to equilibrate for at least 8 h prior to saturated air calibration according to the manufacturer's method. No smoothing of sonde data was performed and data post processing followed NERR protocols (http://cdmo.baruch.sc.edu/data_dissemination.html#NERR%20Water%20Quality%20Data). The Main Channel sonde was located 1 m from the NO_3-DigiScan at approximately the same depth. When sonde data were unavailable, tidal height data were used to estimate the depth of the instrument at the Main Channel site. A YSI Sonde 6600 was used to obtain vertical profiles of temperature and salinity on a cross channel transect at the Main Channel site on September 17, 2003 to verify that waters passing the Main Channel site were well mixed horizontally and vertically.

The NO_3-DigiScan and YSI Sonde 6000 operate independently with the sampling frequency set by internal clocks in each instrument. We observed rapid fluctuations in all water parameters over the course of a few hours so synchronization of the nitrate signal with the Sonde data was crucial for our interpretation. A comparison of the temperature data recorded by both the NO_3-DigiScan and the YSI Sonde (not shown) demonstrated that both clocks remained in synchronization over all deployments.

Daily rainfall and insolation data were obtained from the University of California Statewide Integrated Pest Management Project for a weather station at Pajaro, California (www.ipm.ucdavis.edu/WEATHER/wxretrieve.html). The Pajaro weather station is located 8 km north of Azevedo Pond.

Tidal velocity estimates from tidal stations are not available for Elkhorn Slough and no direct water flow measurements were made during the time period of our observations. Estimates of volumetric water flow at the Main Channel site were derived using the tidal prism versus tidal height relationship determined by Wong (1989). He found that the volumetric flow was related to the change in depth by the equation, Volume flow (10^6 m^3) $= 2.4 \times$ TR, where TR is the tidal range in meters. This relationship has a systematic error because the slough volume has increased by over 30% due to reclamation efforts since the late 1980s. The inaccuracy in the volumetric flow should cause only a

TABLE 1. Average water mass properties of 100 m Monterey Bay (DMB), surface Monterey Bay (SMB), Elkhorn Slough (ES), Salinas River (SR), and the unknown high nitrate water mass. Water volume estimates predict that water flowing past the Main Channel site 2 h after the beginning of the flood tide would be approximately 55% Elkhorn Slough water, 44% surface Monterey Bay water, and 1% Salinas River water. A mixture of 99% 100 m Monterey Bay water and 1% Salinas River water would approximate water properties observed during the high nitrate spikes.

	NO_3 (μM)	Salinity (psu)	DO (μM)	Temp (°C)
Surface Monterey Bay (SMB)	5	33.4	276	12.8
Elkhorn Slough (ES)	15	34.5	175	16.0
Salinas River (SR)	500	24.0	280	15.9
100 m Monterey Bay (DMB)	24	33.8	135	10.0
Unknown High NO_3 Water	30	33.8	125	10.0
Water mass mixing %	Est. NO_3 (μM)	Salinity (psu)	DO (μM)	Temp (°C)
55% ES + 44% SMB + 1% SR	15	34.0	222	14.5
99% DMB + 1% SR	29	33.8	136	10.0

proportional error (our results are low by 30%) but the direction of the flux will be unchanged.

For nitrate flux calculations, hourly nitrate data at the Main Channel site were linearly interpolated to match the time stamp of the depth measurements (taken every 30 min). Nitrate concentrations were then multiplied by the volumetric water transport derived using the tidal prism versus tidal height relationship determined by Wong (1989) to provide nitrate flux at 30-min intervals. Net nitrate transport over the tidal day into and out of Elkhorn Slough was calculated by summing the 30 min nitrate flux estimates past the Main Channel site over a full semidiurnal tidal cycle. Average nitrate concentrations for the flooding and ebbing tide were calculated by taking the mean of the nitrate values observed during the rising tide (low tide to high tide) and falling tide (high tide to low tide). The 30-min linearly interpolated Main Channel nitrate data from March 27 to June 11, 2001 were also used to generate a nitrate power spectrum and a cross correlation function of nitrate and depth.

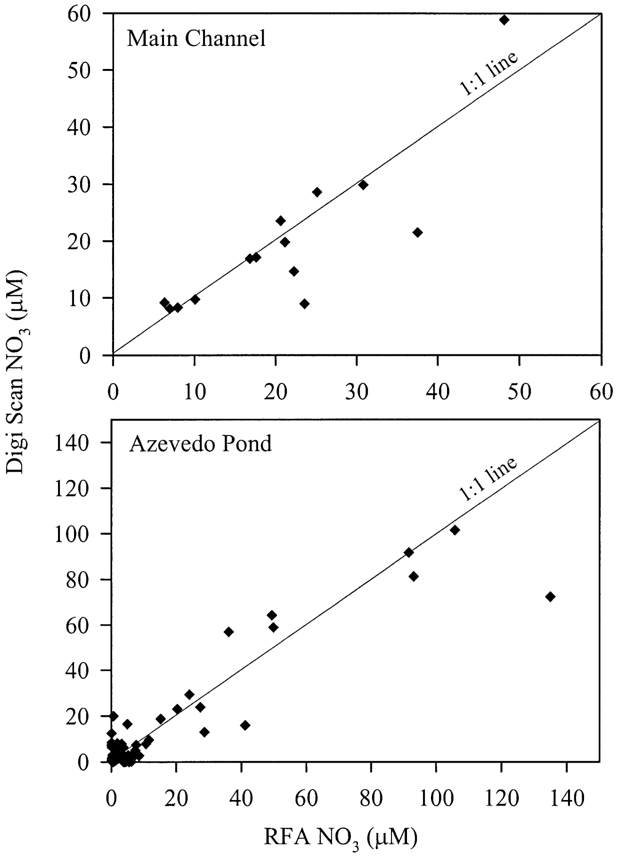

Fig. 3. Comparison of in situ NO_3-DigiScan nitrate results with discrete grab samples analyzed by an Alpkem rapid flow analysis (RFA) nutrient analyzer for the Main Channel site and Azevedo Pond.

The power spectrum for nitrate data collected from March 27 to June 11 at the Outfall Site was calculated with the Applied Statistical Time Series Analysis (ASTSA) program (Shumway and Stoffer 2000; software available at http://anson.ucdavis.edu/~shumway/tsa.html). Before calculation of the spectrum, three 1-h gaps in the data, which were created when the DigiScan was serviced, were filled by linear interpolation. A 1.5 d gap was filled by examining the relationship between nitrate and sensor depth on the previous day and using the observed sensor depth to interpolate nitrate values across the gap. The resulting series of 3,622 data points (30-min intervals) was then padded to 4,096 data points with zeros and the entire series was cosine tapered. The cross correlation function between nitrate and sensor depth was calculated from the unpadded data series using SYSTAT.

Water mass mixing calculations presented in Table 1 use volume estimates from the mouth of Elkhorn Slough to the Main Channel site of 247,500 m^3 (55%) at low tide, 200,000 m^3 (45%) incoming with high tide, and 3,060 m^3 (0.7%) from the Salinas River for a 2 h period (Caffrey 2002).

Comparison of in situ nitrate results with discrete samples verified that our instrument was working properly (Fig. 3). A Model II linear re-

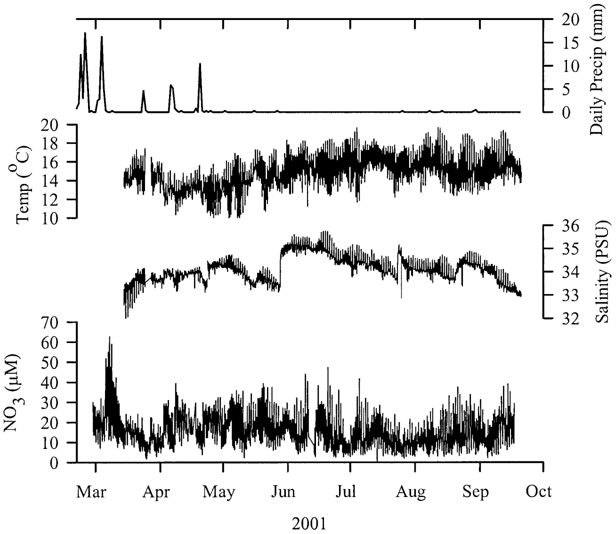

Fig. 4. Seven month record of daily precipitation, temperature, salinity, and hourly NO_3-DigiScan nitrate at the Main Channel site in Elkhorn Slough. Over 4,700 in situ samples were analyzed during this period.

gression of the Azevedo Pond NO_3-DigiScan results versus discrete samples has a slope of 0.92 ± 0.05 (95% CI, $R^2 = 0.94$, $n = 75$) and an intercept of -0.4 ± 1.5 after the elimination of a single large outlier. The Main Channel data regression has a slope of 0.85 ± 0.1 (95% CI, $R^2 = 0.77$, $n = 23$) and an intercept of 2.7 ± 4.0. It should be noted that there was up to a 30 min difference between the times at which the subsamples were collected and the time when the NO_3-DigiScan performed an in situ analysis. Since NO_3 concentrations were changing rapidly over the tidal cycle, especially at the Main Channel site, this sampling time difference accounted for much of the difference observed between the discrete samples and the NO_3-DigiScan results.

Results

NITRATE CONCENTRATIONS AT THE MAIN CHANNEL SITE

Nitrate concentrations at the Main Channel site from March to September 2001 ranged from 5 to 65 μM with an overall average concentration of 14 μM (Fig. 4). Daily precipitation ranged from a maximum of 18 mm d^{-1} during episodic rain events in March and April to no detectable precipitation during the summer months. Average temperature increased from 14°C in the spring to 16°C in the summer before declining in late summer. Main Channel salinity values primarily reflected Monterey Bay surfaces waters, but the conductivity sensor displayed sharp offsets when old instruments were replaced with fresh instruments on May 28 and July 24, 2001. While there is uncertainty in the absolute value of the salinity measurements, we believe the high frequency fluctuations in salinity associated with tidal cycling were real, as discussed below.

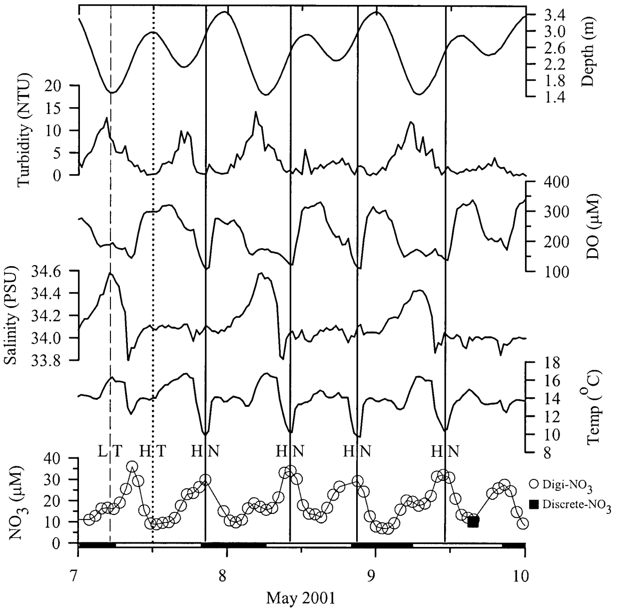

Fig. 5. Depth, turbidity, dissolved oxygen, salinity, temperature, NO_3-DigiScan nitrate, and discrete sample nitrate, from May 7–10, 2001 at Main Channel site. High tide (HT), low tide (LT), and high nitrate water (HN) and associated physical properties are denoted by vertical lines. Bars at bottom indicate day and night.

Nitrate fluctuations at the Main Channel site displayed a strong tidal signal, with distinct nitrate spikes (Fig. 5). The high nitrate pulses observed at the Main Channel were relatively sharp, usually lasting 2–3 h, but these high nitrate pulses were not coincident with the high or low tide. Instead, the maximum nitrate occurred at approximately the mid point of every rising tide and was usually coincident with minima in temperature and dissolved oxygen.

The power spectrum of nitrate observed from March 27 to June 11 at the Main Channel shows sharp peaks near 1.9 and 1 cycle d^{-1}, which clearly track the semidiurnal tides found in Elkhorn Slough (Fig. 6). A cross correlation plot of nitrate and sensor depth indicated that the maximum, negative correlation occurred with a time lag of 2.5 h (low tide precedes maximum nitrate). This negative correlation persisted throughout the March 27 to June 11 period with a strong nitrate pulse near the mid point of each rising tide (Fig. 5).

Nitrate flux calculations assume that the water flowing past the Main Channel site is well mixed both vertically and horizontally. To verify this as-

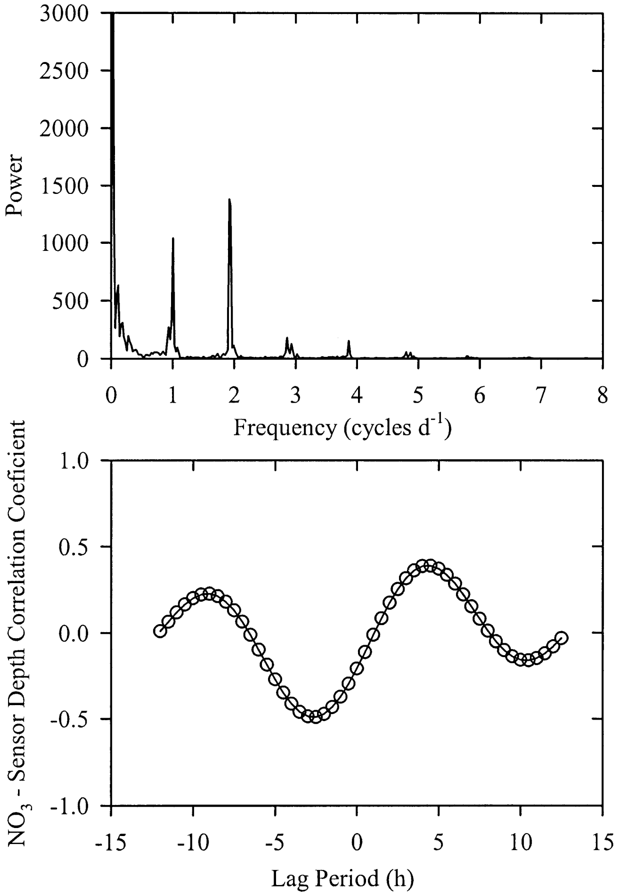

Fig. 6. Nitrate power spectrum and the nitrate-sensor depth cross correlation function at the Main Channel site for data collected from March 27 to June 11, 2001.

sumption, vertical profiles of temperature and salinity from a September 2003 transect across Elkhorn Slough at the Main Channel were collected and showed that the waters at the Main Channel site were well mixed vertically and horizontally (Fig. 7). The profiles of temperature and salinity across the Main Channel that have been obtained to date show that well mixed water appears to be the norm. The calculated average nitrate flux for the April to September 2001 period was 35 kmol N d^{-1} into Elkhorn Slough.

NITRATE CONCENTRATIONS AT AZEVEDO POND

The shallow depth and restricted flow of water in Azevedo Pond generated a large seasonal temperature cycle, with a winter minima of 2°C and summer maxima of over 35°C (Fig. 8). Diel temperature differences were also quite large, up to 10°C during the winter and almost 20°C during the summer. Salinity followed a seasonal cycle with higher salinity during the summer and lower salinity during the winter precipitation periods. Diel salinity changes in Azevedo Pond were less variable than temperature with diel changes of 2–3 psu but salinity could change dramatically in response to the winter precipitation events.

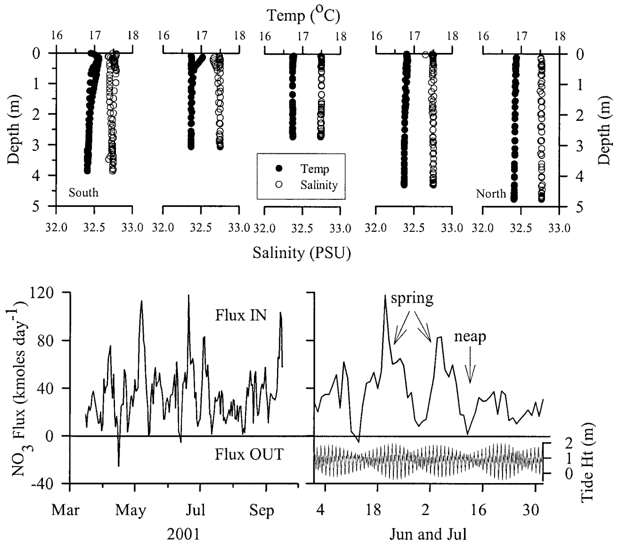

Fig. 7. Vertical profiles of temperature and salinity in a south to north transect at 25-m intervals across Elkhorn Slough beginning at the Main Channel sampling site. Daily nitrate flux from mid March to September 2001 and the June–July detail with tidal height information at the Main Channel site. Positive values represent nitrate flux into Elkhorn Slough from Monterey Bay; negative values are nitrate flux out of Elkhorn Slough to Monterey Bay.

High nitrate concentrations were present in Azevedo Pond during the January–March rainy period for both winter 2000 and winter 2001 and low-

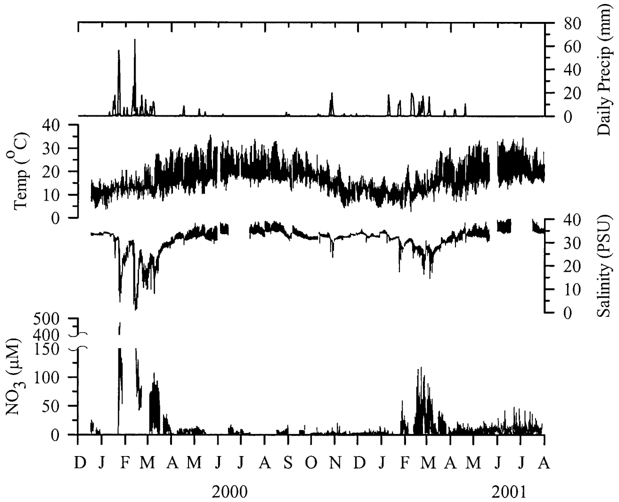

Fig. 8. Twenty month record of daily precipitation, temperature, salinity, and hourly NO$_3$-DigiScan nitrate at Azevedo Pond. Over 9,900 in situ samples were analyzed during this period. Note the scale break in the nitrate axis.

er nitrate values occurred during the rest of the year (Fig. 8). The precipitation and salinity records indicate that winter 2000 had heavier and more sustained precipitation than winter 2001. This interannual difference in precipitation and runoff was reflected in nitrate concentrations with a maximum of 470 μM nitrate observed in winter 2000 compared to a maximum of 120 μM nitrate observed in winter 2001. Nitrate levels in Azevedo Pond remained elevated in February and March 2000 and gradually decreased by the end of March to low values (< 20 μM) at the end of the rainy season. During the April–December 2000 dry period, nitrate concentrations averaged 3 μM with a range of 0 to 20 μM. Short duration precipitation events were observed in October and November 2000, but they were not of sufficient magnitude and duration to mobilize nitrate and concentrations remained low. Increased precipitation in winter 2000–2001 led to increased nitrate concentrations up to 120 μM in February 2001 and nitrate concentrations remained elevated until March 2001.

Discussion

EFFECT OF INTERNAL TIDES ON NITRATE CONCENTRATIONS AT THE MAIN CHANNEL SITE

We have identified 3 primary water masses evident at the Main Channel during each tidal cycle: surface Monterey Bay water with low nitrate and low temperature observed during high tide; Upper Elkhorn Slough water with higher salinity, higher temperature, and low to medium nitrate observed during low tide; and a high nitrate water mass observed during the rising tide (Fig. 5).

During the May 7–10, 2001 period, the high tide brought in cool (13.5°C), less salty (34 psu), oxygenated (275 μM O_2), low nitrate (10 μM) water (Fig. 5). Monthly time series measurements for March to September at a station in the open waters of Monterey Bay 5 km from the mouth of Moss Landing Harbor show that Monterey Bay surface waters have an average temperature, salinity, oxygen, and nitrate signal of 12.5°C, 33.5 psu, 280 μM DO, and 7 μM NO_3, respectively (Pennington and Chavez 2000), consistent with the water mass we observed at high tide. Water with higher salinity (> 34.5 psu), warmer temperature (16°C), medium oxygen (175 μM), and medium nitrate values (15 μM) flowed past the main channel site during low tide. These water properties were consistent with values observed in Upper Elkhorn Slough. A third unknown water mass was present at the mid point of each rising tide with high nitrate (30 μM), low temperature (< 10°C), salinity of 34 psu, and low oxygen (125 μM O_2). The nitrate maximum was not coincident with the turbidity maximum, which occurred on the ebbing tide.

The properties of the high nitrate water mass were not consistent with surface Monterey Bay waters, Upper Elkhorn Slough waters, or Salinas River water (Table 1). The Salinas River is heavily impacted by agricultural nutrient inputs and provides high nitrate (> 400 μM) water that is warmer and less salty than seawater in Moss Landing Harbor (Smith 1973; Caffrey 2002; Johnson 2003). Vertical or horizontal stratification of water flowing past the Main Channel site during the tidal cycle could generate the nitrate and physical parameter time series that we observed but temperature and salinity profiles from September 2003 indicated that water at the Main Channel site was well mixed both vertically and horizontally (Fig. 7). Water volume estimates predicted that water flowing past the Main Channel site 2 h after the beginning of the flood tide would be 55% Elkhorn Slough water remaining from the previous ebb tide, 44% surface Monterey Bay water coming in with the flood tide, and 1% Salinas River water (Table 1). Conservative mixing of these three source waters yield water characteristics of 14.5°C, 34.0 psu, 220 μM DO, and 14.8 μM NO_3, properties that were quite different from the unknown water observed during the high nitrate spikes. The low temperature, low oxygen, and high nitrate characteristics of the high nitrate spikes could not be duplicated by any mixture of Elkhorn Slough, surface Monterey Bay, and Salinas River waters.

The high nitrate pulses at the Main Channel site were coincident with sharp fluctuations in the independently measured temperature and oxygen (Fig. 5). The temperature, salinity, and oxygen characteristics of the high nitrate water mass observed at the Main Channel site were consistent with average water properties observed at 100 m in Monterey Bay over a 12 yr period (average 10°C, range 7.8–15.7°C; average 33.8 psu, range 33.2–34.1 psu; average 135 μM DO, range 78–264 μM DO; average 24 μM NO_3, range 4–32 μM NO_3, respectively; Pennington and Chavez 2000). Seasonal upwelling in Monterey Bay leads to large changes in water properties at 100 m depth but deep Monterey Bay water was the only water mass we identified that could provide the requisite water volume and temperature, salinity, and oxygen characteristics we observed during the high nitrate spikes. These observations lead us to conclude that deep Monterey Bay water was the primary source for the high nitrate signals observed at the Main Channel site.

The timing of the high nitrate spikes at the mid point of the rising tide provided a clue to the origin of the unknown water mass. Semidiurnal internal tides with amplitudes from 30 to 120 m propagate as a tidal bore up the Monterey Submarine Canyon (Shea and Broenkow 1982; Heard 1992; Breaker and Broenkow 1994; Petruncio et al. 1998; Rosenfeld et al. 1999). Our data indicate the internal tide continued past the head of Monterey Canyon and into Elkhorn Slough and these large amplitude internal tides were the most likely mechanism for generating these mid-tide high nitrate pulses. Internal tide effects in Elkhorn Slough were observed in data collected in 1999 during a thermal study of the Moss Landing Power Plant (Duke Energy 2000). In the Duke Energy study, a series of temperature recorders located outside the mouth of Moss Landing Harbor, inside the harbor, and at the Main Channel station showed a clear progression of colder subsurface water from outside Moss Landing Harbor, into and through the harbor, and up past the Main Channel station. Low temperature water was observed at the Main Channel site at the mid point of the rising tide, consistent with our observations.

The consistency of the high nitrate signal, observed on almost every rising tide over a 7 mo period, indicates that there is a direct connection with the Monterey Submarine Canyon internal tide. Nitrate concentrations above 35 μM are rarely observed in Monterey Bay water less than 200 m (Pennington and Chavez 2000) and a small amount of additional nitrate most likely came from the warm high nitrate groundwater or Salinas River water that enters the southern end of Moss Landing Harbor.

Conservative mixing of 99% 100 m Monterey Bay water with 1% of Salinas River water would produce water properties very similar to the unknown water mass observed during the high nitrate spikes (Table 1). Small changes in nitrate loading from the Salinas River would have significant impacts on the nitrate flux into Elkhorn Slough but the vast majority, 80–90%, of the total nitrate load into Elkhorn Slough during this May 2001 period appears to come from 100 m Monterey Bay water. The temperature, salinity, oxygen, and nitrate concentrations, as well as the timing of the high nitrate signal, lead us to conclude that an internal tidal wave originating in Monterey Submarine Canyon was the primary source for the high nitrate signals that we observed at the Main Channel site.

NITRATE FLUXES AT THE MAIN CHANNEL SITE

Elkhorn Slough appeared to be a large nitrate sink from mid March to July 2001. The average of all nitrate measurements on the flooding tide was 18 ± 8 μM versus 11 ± 6 μM on the ebbing tide at the Main Channel site. The average of all nitrate measurements during the mid March–July 2001 period was 14 μM for the Main Channel site and 8 μM at Azevedo Pond, indicating that nitrate was lost as water reached the upper slough.

The estimated nitrate transport past the Main Channel site into Elkhorn Slough during the dry season nearly always exceeded transport out of Elkhorn Slough when averaged over the tidal day. Elkhorn Slough consumed an average of 35 kmol N d^{-1} from mid March to July 2001 (Fig. 7). When this nitrate transport is averaged over the area of the slough, it represents a nitrate loss of 4 mmol m^{-2} d^{-1}. The peaks observed in the nitrate flux were due to the spring-neap tidal cycle effect on water volume flow into and out of Elkhorn Slough. The increasing tidal range during the spring tide periods caused a larger flux of water and nitrate into the slough. Nitrate transport then decreased as the tidal range moved to neap conditions and there was net water transport from the slough.

There was little precipitation during the time that we deployed the nitrate sensor at the Main Channel site but a significant amount of nitrate is predicted to export from Elkhorn Slough to Monterey Bay during the rainy season. We did monitor nitrate during one large precipitation event at the Main Channel site in early March 2001, but salinity and depth data from the sonde were not available for this period. The precipitation event from March 3–5, 2001 generated a high nitrate pulse that was observed at Azevedo Pond during the high tide and several hours later at the Main Channel site during the low tide (Fig. 9). Only during this one period in early March 2001 did we observe higher nitrate on the ebb tide (average 50 μM) than the flood tide (average 15 μM) at the Main Channel site. High nitrate waters (35–120 μM NO_3) were observed in Carneros Creek 5 km upstream of Elkhorn Slough during early March 2001 (Los Huertos et al. 2001) indicating that Carneros Creek was a possible source of some of the high nitrate pulse recorded at Azevedo Pond. While we could not calculate a nitrate flux at the Main Channel site for this rain event, we believe these high nitrate waters in Upper Elkhorn Slough eventually flowed through Elkhorn Slough and exported nitrate from Elkhorn Slough to Monterey Bay.

NITRATE UPTAKE AT THE MAIN CHANNEL SITE

Nitrate must be lost from Elkhorn Slough by denitrification or by plant nitrate uptake though we cannot distinguish between these two processes with our data set. Nutrient uptake by benthic autotrophs and heterotrophs and subsequent burial in the sediments and wetland substrate can be a large sink for nitrogen, consuming up to 80% of the available inorganic nitrogen input in estuaries

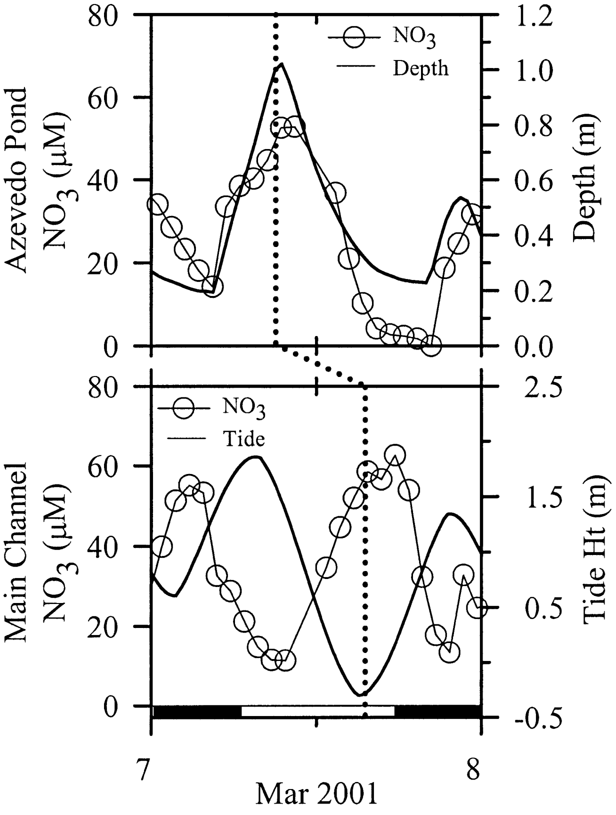

Fig. 9. Nitrate (o) and tide height (———) or depth for the March 7–8, 2001 rainy period at the Main Channel and Azevedo Pond. Bars at bottom indicate day and night. The dotted line marks the high nitrate high tide water observed at Azevedo Pond during high tide that was eventually observed at the Main Channel site during low tide, indicating a flux of nitrogen out of Elkhorn Slough and into Monterey Bay.

(Smith et al. 1985; Risgaard-Petersen et al. 1998; Kremer et al. 2000). Denitrification, primarily in the sediments, is also a sink for nitrogen in most estuarine systems, removing 35–40% of nitrogen inputs to estuaries (Seitzinger 1988, 2000; Jickells 1998). Estimates of denitrification in estuarine and coastal sediments are typically < 1 mmol m^{-2} d^{-1} (Seitzinger 1988, 2000). Caffrey et al. (2002) observed average denitrification rates of 1.2 mmol m^{-2} d^{-1} (range 0–11 mmol m^{-2} d^{-1}) in Elkhorn Slough. Our calculated nitrate loss rate for the entire slough of 4 mmol m^{-2} d^{-1}, based on the nitrate balance observed at the Main Channel site, is higher than the average denitrification rate of 1.2 mmol m^{-2} d^{-1} observed in Elkhorn Slough suggesting that perhaps 30% of the nitrate was consumed by denitrification and 70% of the nitrate was consumed by photosynthetic uptake. Some of the nitrate loss may be balanced by ammonium or organic nitrogen export, which we did not monitor.

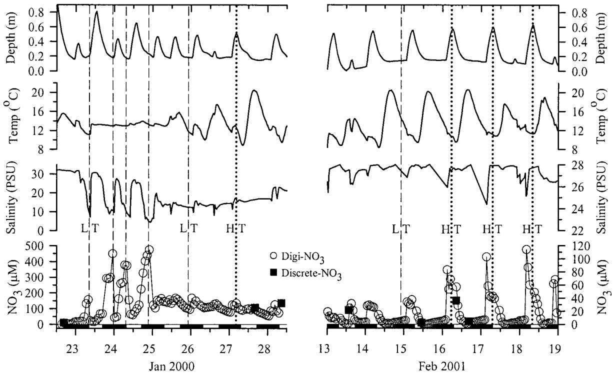

Fig. 10. Depth, temperature, salinity, and NO_3-DigiScan nitrate and discrete sample nitrate, for January 22–28, 2000 and February 13–19, 2001 at Azevedo Pond. HT (·······) and LT (– – –) indicate high and low tides, bars at bottom indicate day and night. Note the different scales for nitrate and salinity during the two periods.

NITRATE SOURCES IN AZEVEDO POND

Our results demonstrate that there were two major sources of high nitrate in Azevedo Pond; nitrate runoff from the strawberry field directly surrounding Azevedo Pond and nitrate brought from Upper Elkhorn Slough by the incoming tide. The incoming high tide can either add nitrate to Azevedo Pond or dilute the nitrate already there. For most of the year, nitrate values in Azevedo Pond were lower than in the mainstem of Upper Elkhorn Slough indicating that the incoming high tide flushed Azevedo Pond with higher nitrate water. Instruments at Azevedo Pond recorded large winter precipitation events in both 2000 and 2001, and we will examine one event in late January 2000 and one event in February 2001 to contrast the effects of precipitation events (Fig. 10).

On January 23, 2000, an initial pulse of freshwater runoff was observed in concert with a rapid drop in salinity from 31 to 7 psu during the low tide period (Fig. 10). The stormy and cloudy conditions reduced the solar flux to Azevedo Pond and decreased the normal temperature difference between water in Azevedo Pond and Upper Elkhorn Slough resulting in a flat temperature signal observed during the storm (January 23–25). Nitrate appeared to be mobilized directly from the strawberry fields draining into Azevedo Pond during this rain event and the nitrate levels increased from 15 μM to over 100 μM in 3 h on January 23 during low tide. The next incoming high tide brought high salinity, lower nitrate water from the Upper Elkhorn Slough into Azevedo Pond and nitrate levels decreased to 15 μM while salinity rose to 30 psu. The subsequent low tide showed another strong freshwater runoff event and salinity values dropped from 30 to 10 psu while nitrate levels increased 30-fold from 15 μM to over 450 μM during the low tide period. The next incoming high tide then brought in high salinity water with a nitrate level of 45 μM, evidence that the nitrate concentrations in Upper Elkhorn Slough were increasing as well. The relative magnitude of the tidal nitrate pulsing decreased after January 25 as both Azevedo Pond and the Upper Elkhorn Slough had accumulated elevated nitrate. After passage of the storm (January 25), water temperature differences between Azevedo Pond and Upper Elkhorn Slough were reestablished and the effects of tidal cycling on water temperature in Azevedo Pond resumed. Discrete nitrate samples taken on January 22, 27, and 28 contained 10 to 135 μM NO_3 and agree well with the NO_3-DigiScan results. The relatively low temporal resolution of the discrete samples completely missed the extreme nitrate event and strong tidal forcing observed from January 23–25, 2000.

Precipitation events in winter 2001 were less able to mobilize nitrate from fields immediately surrounding Azevedo Pond and did not lead to high nitrate concentrations during low tide periods as observed in January 2000 (Fig. 10). High nitrate and lower salinity water from Upper Elkhorn Slough flooded into Azevedo Pond at the beginning of the high tide, indicating that surface or groundwater inputs of high nitrate occurred in other parts of Elkhorn Slough and not in the fields surrounding Azevedo Pond. Discussions with local farmers indicated that farming practices on the land surrounding Azevedo Pond changed between winter 2000 and winter 2001. During winter 2000, strawberry crops were grown and fertilized while during winter 2001, cover crops were planted and no fertilizers were applied. Only during a few high precipitation events in the wet winter of 2000 did we find evidence of nitrate input directly from agricultural fields surrounding Azevedo Pond. This suggests that most precipitation events were not mobilizing nitrate directly from adjacent agricultural fields into Azevedo Pond but that surface or groundwater agricultural runoff in other regions of Elkhorn Slough were the source of higher nitrate waters.

Diel Cycling and Nitrate Uptake in Azevedo Pond

In contrast to the nitrate signal observed at the Main Channel site, nitrate concentrations in Azevedo Pond during the spring-summer-fall period were generally in phase with the tidal cycle with the highest nitrate concentrations coincident with the high tide and the lowest nitrate during the low tide. The effects of tidal cycling on nitrate, dissolved oxygen, salinity, temperature, and depth observed during September 17–20, 2000 were typical during the dry summer and fall in Azevedo Pond (Fig. 11). Temperature and salinity fluctuations (10°C and 3 psu) were the result of diel cycles in solar insolation, evaporation, and high tide injection of Upper Elkhorn Slough water. High tide injected Upper Elkhorn Slough water near saturation with dissolved oxygen, and oxygen levels often increased in the late afternoon to over 300 μM DO (> 150% saturation) presumably due to photosynthesis. Oxygen levels declined to values < 10 μM during the evening and hypoxic conditions remained until the next high tide flushed the pond with higher oxygen water and higher nitrate or until daytime when increased light levels stimulated photosynthesis, which recharged the oxygen levels. During neap tides, the lower high tide is not high enough to significantly flood Azevedo Pond and the resulting quiescent conditions can create hypoxic conditions that last for more than 6 h. Nitrate concentrations in Azevedo Pond increased rapidly during the incoming tide to a maximum coincident with the high tide and decreased during the falling tide. High tide injection of nitrate during the daytime appeared to stimulate photosynthesis resulting in an increase in DO concentrations in the afternoon. In Azevedo Pond, this phenomena of rapid and dramatic changes in diel oxygen from supersaturated to depleted levels in response to nutrients, sunlight, and tidal cycle has been

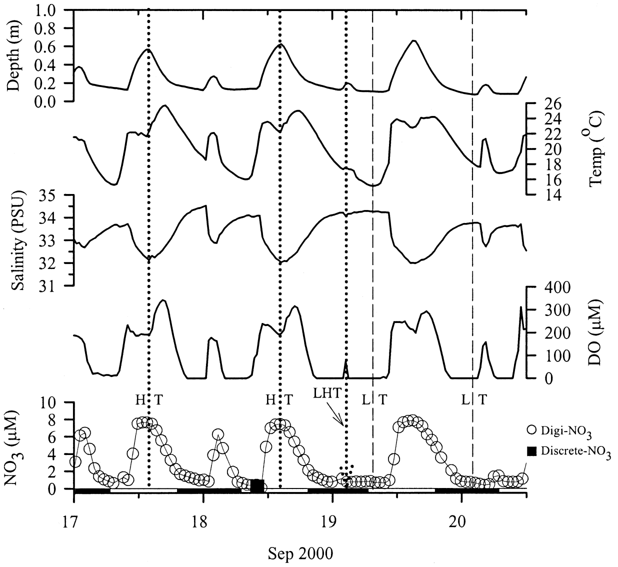

Fig. 11. Depth, temperature, salinity, dissolved oxygen, and nitrate from September 17–20, 2000 at Azevedo Pond. LT (– – –), HT (········), and LHT indicate low, high, and low-high tides, bars at bottom indicate day and night. Note the long quiescent periods during the evenings of September 19–20 when the lower high tide did not vigorously flush Azevedo Pond with new water.

TABLE 2. Estimated primary productivity (average, standard error, 10th and 90th percentile) and autotrophic nitrate uptake rates in Azevedo Pond for different C:N ratios.

	Estimated Primary Productivity (mmol C m^{-2} d^{-1})	Calculated N Uptake for a C:N of 10 (mmol N m^{-2} d^{-1})	Calculated N Uptake for a C:N of 6.6 (mmol N m^{-2} d^{-1})
Average	273	27	41
Standard error	5	0.5	0.8
10th percentile	119	12	18
90th percentile	430	43	65

termed hyperventilation (Beck and Bruland 2000; Beck et al. 2001).

Estimates of nitrate consumption in Azevedo Pond for the September 19–20, 2000 period were calculated from the slope of nitrate versus time during the > 6 h low tide quiescent periods when tidal exchange was at a minimum (Fig. 11). This estimate does not take into account water column stratification that does occur during long quiescent periods and is only meant to provide a rough estimate of the nitrate loss in Azevedo Pond in relation to other nitrate cycling processes. Our calculations suggest a nitrate loss rate of 0.2 $\mu M\ h^{-1}$, which corresponds to a nitrate loss of 3 mmol NO_3 m^{-2} d^{-1} for a mean pond depth of 0.8 m. This apparent decrease in nitrate during the low tide period could be attributed to denitrification in the sediments or uptake by photosynthetic and benthic organisms.

Azevedo Pond has an abundant flora during the summer and fall months with thick algal mats of *Enteromorpha* sp. and *Ulva* sp. that can completely cover the bottom (Caffrey et al. 2003). Estimated average primary production calculated from the Azevedo Pond dissolved oxygen data, using the method described by Odum and Hoskins (1958), was 270 mmol C m^{-2} d^{-1} (Caffrey 2003). Benthic algae such as *Enteromorpha* sp. and *Ulva* sp. can have carbon:nitrogen (C:N) ratios from 6 to 10 (Trimmer et al. 2000), so photosynthetic nitrogen demands calculated with C:N ratios of 6.6 and 10 provide a range of photosynthetic nitrogen demand estimates (Table 2). The calculated nitrogen demand for an estimated primary production of 270 mmol C m^{-2} d^{-1} (Caffrey 2003), was 41 mmol N m^{-2} d^{-1} for a C:N of 6.6 and 27 mmol N m^{-2} d^{-1} for a C:N of 10. Our estimated nitrogen demand of 27–41 mmol N m^{-2} d^{-1} is much higher than previous estimates of denitrification rates in Azevedo Pond (1 mmol N m^{-2} d^{-1}; Caffrey 2003), suggesting that nitrate dynamics are likely dominated by autotrophic nitrogen uptake. Further research is needed to evaluate the relative importance of nutrient uptake by different autotrophic communities (macroalgae, benthic algae, and phytoplankton) in Elkhorn Slough.

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LITERATURE CITED

BECK, N. G. AND K. W. BRULAND. 2000. Diel biogeochemical cycling in a hyperventilating shallow estuarine environment. *Estuaries* 23:177–187.

BECK, N. G., A. T. FISHER, AND K. W. BRULAND. 2001. Modeling water, heat, and oxygen budgets in a tidally dominated estuarine pond. *Marine Ecology Progress Series* 217:43–58.

BOYNTON, W. R., J. H GARBER, R. SUMMERS, AND W. M. KEMP. 1995. Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries* 18:285–314.

BREAKER, L. C. AND W. W. BROENKOW. 1994. The Circulation of Monterey Bay and Related Processes. *Oceanography and Marine Biology Annual Review* 32:1–64.

BREWER, P. G. AND J. P. RILEY. 1965. The automatic determination of nitrate in seawater. *Deep-Sea Research* 12:765–772.

CAFFREY, J. M. 2002. Biogeochemical Cycling, p. 211–233. *In* J.M. Caffrey, M. Brown, B. Tyler, M. Silberstein (eds.), Changes in a California Estuary: An Ecosystem Profile of Elkhorn Slough. Chapter 12. Elkhorn Slough Foundation. Moss Landing, California.

CAFFREY, J. M. 2003. Production, Respiration and Net Ecosystem Metabolism in U.S. Estuaries. *Environmental Monitoring and Assessment* 81:207–219.

CAFFREY, J. M. AND W. BROENKOW. 2002. Hydrology, p. 31–46. *In* J. M. Caffrey, M. Brown, B. Tyler, M. Silberstein (eds.), Changes in a California Estuary: An Ecosystem Profile of Elkhorn Slough. Chapter 4. Elkhorn Slough Foundation. Moss Landing, California.

CAFFREY, J. M. AND J. W. DAY JR. 1986. Control of the variability of nutrients and suspended sediments in a Gulf Coast estuary by climatic forcing and spring discharge of the Atchafalaya River. *Estuaries* 9:295–300.

CAFFREY, J. M., N. E. HARRINGTON, I. SOLEM, AND B. B. WARD. 2003. Biogeochemical Processes in a Small California estuary: 2. Nitrification Activity, Community Structure and Role in Nitrogen Budgets. *Marine Ecology Progress Series* 248:27–40.

CAFFREY, J. M., N. HARRINGTON, AND B. WARD. 2002. Biogeochemical processes in a small California estuary: 1. Benthic flux and pore water constituents reflect high nutrient freshwater inputs. *Marine Ecology Progress Series* 233:39–53.

DUKE ENERGY. 2000. Final report: Evaluation of proposed discharge system with respect to the thermal plan. *In* Moss Landing power plant modernization project. Duke Energy Moss Landing LLC, Moss Landing, California.

GLASGOW, H. B. J. AND J. M. BURKHOLDER. 2000. Water quality trends and management implications from a five-year study of a eutrophic estuary. *Ecological Applications* 10:1024–1046.

HEARD, A. J. 1992. A Kinematic Model of Baroclinic Tidal Currents at the Head of Monterey Submarine Canyon. M.S. Thesis, San Jose State University, San Jose, California.

HUBERTZ, E. D. AND L. B. CAHOON. 1999. Short-term variability of water quality parameters in two shallow estuaries of North Carolina. *Estuaries* 22:814–823.

JICKELLS, T. 1998. Nutrient biogeochemistry of the coastal zone. *Science* 281:217–222.

JOHNSON, K. S. 2003. State of Technology in the Development and Application of Nutrient Sensors. Alliance for Coastal Technology Workshop, http://www.actonline.ws/Download/Nutrient_Sensor_Report.pdf)

KREMER, J. N., W. M. KEMP, A. E. GIBLIN, I. VALIELA, S. P. SEITZINGER, AND E. E. HOFFMAN. 2000. Linking biogeochemical processes to higher trophic levels, p. 299–341 *In* J. Hobbie (ed.), Estuarine science: A synthetic approach to research and practice. Island Press. Washington, D.C.

LOS HUERTOS, M., L. E. GENTRY, AND C. SHENNAN. 2001. Land use and stream nitrogen concentrations in agricultural watersheds along the Central Coast of California. *The Scientific World Journal* 1:615–622

MALZONE, C. M. 1999. Tidal scour and its relation to erosion and sediment transport in Elkhorn Slough. M.S. Thesis, San Jose State University, San Jose, California.

NATIONAL RESEARCH COUNCIL (NRC). 2000. Clean Coastal Waters: Understanding and reducing the effects of nutrient pollution. National Academy Press, Washington, D.C.

NIXON, S. W. 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia* 41:199–219.

NIXON, S. W., S. L. GRANGER, AND B. L. NOWICKI. 1995. An assessment of the annual mass balance of carbon, nitrogen, and phosphorus in Narragansett Bay. *Biogeochemistry* 31:15–61.

ODUM, H. T. AND C. M. HOSKINS. 1958. Comparative studies on the metabolism of marine waters. Publications of the Institute of Marine Science University of Texas, 5:16–46.

PENNINGTON, J. T. AND F. P. CHAVEZ. 2000. Seasonal fluctuations of temperature, salinity, nitrate, chlorophyll, and primary production at station H3/M1 over 1989–1996 in Monterey Bay, California. *Deep-Sea Research* 47:947–973.

PETRUNCIO, E. T., L. K. ROSENFELD, AND J. D. PADUAN. 1998. Observations of the internal tide in Monterey Canyon. *Journal of Physical Oceanography* 28:1873–1903.

RABALAIS, N. N., R. E. TURNER, D. JUSTIC, Q. DORTCH, W. J. WISEMAN, AND B. K. SEN GUPTA. 1996. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. *Estuaries* 19:386–407.

RISGAARD-PETERSEN, N., T. DALSGAARD, S. RYSGAARD, P. B. CHRISTENSEN, J. BORUM, K. MCGLATHERY, AND L. P. NIELSEN. 1998. Nitrogen balance of a temperate eelgrass *Zostera marina* bed. *Marine Ecology Progress Series* 174:281–291.

ROSENFELD, L. K., J. D. PADUAN, E. T. PETRUNCIO, AND J. E. GONCALVES. 1999. Numerical Simulations and Observations of the Internal Tide in a Submarine Canyon. http://www.oc.nps.mil/~radlab/LIWI/aha99rosenfeld.pdf.

SAKAMOTO, C. M., G. E. FRIEDERICH, AND L. A. CODISPOTI. 1990. MBARI Procedures for Automated Nutrient Analyses Using a Modified Alpkem Series 300 Rapid Flow Analyzer. MBARI Technical Report No. 90-2. Moss Landing, California.

SEITZINGER, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnology and Oceanography* 33:702–724.

SEITZINGER, S. P. 2000. Scaling Up: Site specific measurements to Global-scale estimates of denitrification, p. 211–240. *In*: J. E. Hobbes (ed.), Estuarine science: A synthetic approach to research and practice. Island Press. Washington, D.C.

SHEA, R. E. AND W. W. BROENKOW. 1982. The Role of Internal Tides in the Nutrient Enrichment of Monterey Bay, California. *Estuarine and Coastal Shelf Science* 15:57–66.

SHUMWAY, R. H. AND D. S. STOFFER. 2000. Time Series Analysis and its Applications (Springer Texts in Statistics). Springer-Verlag, New York, New York.

SMITH, R. E. 1973. The hydrography of Elkhorn Slough, a shallow California Coastal Embayment. Technical Publication 73-2, Moss Landing Marine Laboratories, Moss Landing, California.

SMITH, C. J., R. D. DELAUNE, AND W. H. PATRICK. 1985. Fate of Riverine Nitrate Entering an estuary: 1. Denitrification and Nitrogen Burial. *Estuaries* 8:15–21.

TRIMMER, M., D. B. NEDWELL, D. B. SIVYER, AND S. J. MALCOLM. 2000. Seasonal organic mineralization and denitrification in intertidal sediments and their relationship to the abundance of Enteromorpha sp. and Ulva sp. *Marine Ecology Progress Series* 203:67–80.

VARNEY, M. S. 2000. Chemical Sensors in Oceanography. Ocean Science and Technology, 1. Gordon and Breach Science Publishers, Amsterdam, The Netherlands.

VITOUSEK, P. M., J. D. ABER, R. W. HOWARTH, G. E. LIKENS, P. A. MATSON, D. W. SCHINDLER, W. H. SCHLESINGER, AND D. G. TILMAN. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7:737–750.

WEEKS, D. A. AND K. S. JOHNSON. 1996. Solenoid pumps for flow injection analysis. *Analytical Chemistry* 68:2717–2719.

WONG, C. R. 1989. Observations of tides and tidal currents in Elkhorn Slough. M.S. Thesis, San Jose State University, San Jose, California.

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