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Instruments and Methods

Diel nitrate cycles observed with in situ sensors predict monthly and annual new production

Kenneth S. Johnson*, Luke J. Coletti, Francisco P. Chavez

Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039, USA

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Abstract

We report on a direct and autonomous measure of new production based on time series observations with ISUS nitrate sensors deployed for several years on oceanographic moorings offshore of Monterey Bay, California. The amplitude of diel cycles of surface nitrate is correlated with rates of primary production measured by ^{14}C uptake. The drawdown of nitrate averaged over a year is about 70% of the fixed nitrogen needed for biomass production. Phytoplankton biomass predicted from the diel nitrate uptake and a fixed rate constant for nitrate loss (grazing and export) matched observations over the annual cycle. New production rates determined with the moored sensors are highly correlated with nitrate concentration and the intensity of upwelling. The implication is that arrays of moorings with chemical sensors can now be used to estimate new production of biomass and ecosystem processes over multiple temporal and spatial scales.

Keywords: Nitrates; Moorings; Primary production; Upwelling; Monterey bay; Nitrate sensor

1. Introduction

The quality and quantity of primary production determines the fate of chemical elements and the overall character of an ecosystem (Marra, 2002). In the ocean, the measurement of primary production is problematic for several reasons. First, the measurements are tedious and time consuming, requiring incubation of samples over several hours to a day. Careful techniques are required, given that contamination inhibits photosynthesis (Fitzwater et al., 1982). Secondly, the standard ^{14}C uptake measurement is ambiguous, giving a number that is less than gross, but more than net photosynthesis (Marra, 2002). As a result, there are few long-term records of primary production and none with temporal resolution that approaches daily over extended time periods.

The daily cycle of photosynthesis in the surface ocean drives diel changes in the concentrations of chemicals, including oxygen, inorganic carbon and particulate organic carbon, that are consumed or produced as plants grow and new biomass is created (Siegel et al., 1989; Chipman et al., 1993; Degrandpre et al., 1998). These cycles have not been widely used to determine primary production because of: (1) the paucity of robust autonomous sensors, and (2) the difficulty in sustaining long-term chemical and biological sensor deployments in the ocean. Nitrate is a particularly attractive

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*Corresponding author. Tel.: +1 831 775 1985;
fax: +1 831 775 1620.
E-mail address: johnson@mbari.org (K.S. Johnson).

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element to focus on given that it is the primary source of "new" nitrogen (sensu Dugdale and Goering, 1967) and nitrogen may be the limiting nutrient on a global scale. Photosynthetically driven changes in nitrate concentration have been observed over daily periods with shipboard measurements (Ryther et al., 1961; Eppley and Renger, 1988; Zhang et al., 2001). The ratio of C–N in phytoplankton is constrained to a fairly narrow range (Falkowski, 2000) near the Redfield ratio (Redfield et al., 1963) of 6.6:1, which links nitrate uptake directly to new production as defined by Dugdale and Goering (1967). The seasonal depletion of nitrate in the upper ocean has been used as an indicator of new production at high latitudes and in upwelling regions (Wong et al., 2002; Rubin, 2003).

Optical nitrate sensors (in situ ultraviolet spectrophotometers (ISUS)) have already been shown to be capable of long-term deployment in the ocean (Johnson and Coletti, 2002). Here we present data from ISUS nitrate sensors deployed on moorings at 20 and 50 km offshore of Monterey Bay on the central California coast (Chavez et al., 1997). Monterey Bay is a region where the circulation and physical supply of nitrate are dominated by upwelling (Breaker and Broenkow, 1994; Pennington and Chavez, 2000). We use the diel cycles of nitrate observed with the ISUS instruments to calculate new production. We examine the variability of new production over multiple years and the processes that regulate this variability in the offshore California region.

2. Methods

Nitrate was measured at 1 m depth using ISUS nitrate sensors (Johnson and Coletti, 2002) on the M1 (20 km offshore, 1200 m depth) and M2 (50 km offshore, 1800 m depth) moorings offshore of Monterey Bay (Fig. 1). The mooring data, including the complete ultra-violet spectrum measured by ISUS, are telemetered to shore hourly (Chavez et al., 1997). Nitrate concentrations are calculated using the measured light absorption spectrum from 217 to 240 nm and a linear baseline estimate. Biofouling of the optics was inhibited with a copper

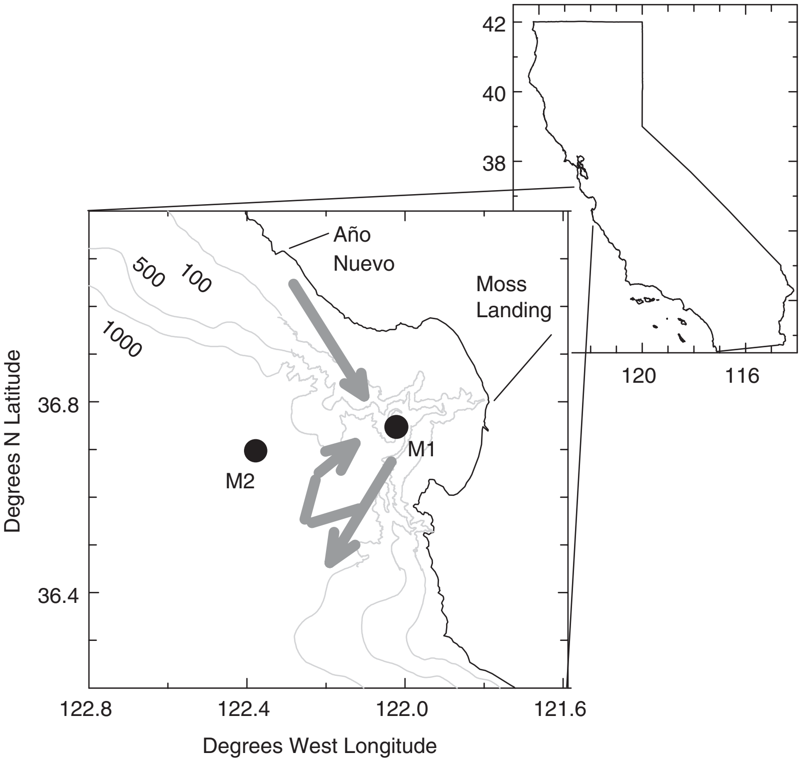

Fig. 1. Mooring locations (M1: 36.747°N, 122.022°W, 1200 m depth and M2: 36.697°N, 122.378°W, 1800 m depth) offshore of Monterey Bay. Northern arrow shows the trajectory of upwelled water from its source south of Point Año Nuevo. Southern arrow shows the mean flow out of the Bay and the periodic recirculation during relaxation of upwelling favorable winds (not to scale). Depth contours in m.

and Nitex shield. Fouling of the instrument is diagnosed quantitatively by examining the residual differences between the observed absorption spectra and the fitted model. Data are rejected when the standard deviation of the absorbance residuals increased to values greater than 0.005.

Observations were made on the M1 mooring from 22 February 2002 to 22 October 2004 and from 3 July 2002 to 11 December 2004 on the M2 mooring. Deployments at M1 produced 640 days of useful data during the 973 days interval. There are 578 days of data at M2 during the 892 days interval. The ISUS nitrate concentrations are accurate to $\pm 2\,\mu M$ (standard error of estimate for regression versus bottle samples), while the precision of the measurements determined from observations over day-long periods during quiescent conditions is $\pm 0.15\,\mu M$ (1 SD). Long-term sensor drift may result in negative nitrate concentrations with values as low as $-2\,\mu M$ during periods when the real nitrate concentration is near zero. We have not corrected the data for long-term drift and the negative values do not affect any of the conclusions reported here.

Spectral radiometers were placed at 10 m depth on the mooring line and on the mooring tower. The measurements at 10 min intervals were binned to hourly averages and chlorophyll concentrations were estimated from the attenuation of sunlight at 490 nm (Morel, 1988). The radiometers were protected from fouling with a copper shutter (Chavez et al., 2000). Discrete water samples have been collected near each mooring since 1989 at approximately 3-week intervals (Pennington and Chavez, 2000). These samples are analyzed for ^{14}C primary production (24-h incubations), nitrate and extracted chlorophyll.

3. Results and discussion

3.1. Annual variability

A year of wind, surface temperature, nitrate and chlorophyll data from M1 sensors are shown in Figs. 2(A)–(D). Gaps in the data sequence are due to biofouling of optical surfaces and instrumental failures. In most cases, when these failures were detected in the telemetered data, a visit to the mooring was required to clean the optical surfaces or to replace the faulty instrument. Occasionally, an air bubble that formed on the optics would clear itself.

Measurements of nitrate and chlorophyll concentration made on discrete samples collected at 0.5–1 km distance from the mooring are shown as red circles in Fig. 2(C) and (D). A Model II regression line (Laws, 1997) was fitted to the paired mooring ISUS and discrete sample nitrate data collected near M1 over the past 2 years (Fig. 3). It indicates no significant difference between in situ measurements and conventional autoanalyzer measurements ($NO_3\text{-ISUS} = 0.1[\pm 1.2] + 0.98[\pm 0.16] \times NO_3\text{-bottle}$, 95% CI). The standard error of the regression line is $\pm 2\,\mu M$, which is about the accuracy limit of the instrument. Some of the scatter is undoubtedly also due to small-scale variability of nitrate in surface waters (KJ, unpublished data). The precision of the data is much better than $\pm 2\,\mu M$ over 1 day. During periods with low nitrate, the standard deviation of all data collected on 1 day may be as small as $\pm 0.15\,\mu M$.

The classical picture of nutrient cycling at mid-latitudes is characterized by a winter maximum and summer depletion (e.g. Harvey, 1928). The seasonal cycle differs in the Monterey Bay region because the major signal is driven by upwelling and not by deep winter mixing. Shipboard sampling in Monterey Bay at near monthly intervals shows an annual cycle of nitrate that is characterized by a maximum in late spring (Pennington and Chavez, 2000), which is the time of maximum upwelling (Fig. 4). Nitrate is depleted to a concentration of a few micromolar during the remainder of the year. This pattern is reproduced in the mooring measurements when the hourly data is binned to monthly averages (Fig. 4). However, the hourly data (Fig. 2) show a more complex pattern that is produced by episodes of upwelling favorable wind that occur with a time scale of several days to several weeks (Service et al., 1998; Pennington and Chavez, 2000; Fitzwater et al., 2003). The interaction of wind and the Earth's rotation during the episodic, southeasterly winds results in net transport of surface waters away from the coast and cold, nitrate-rich water comes to the surface (Figs. 2(A)–(C)). These episodes of upwelling are interspersed by reversals in wind direction that produce downwelling events with onshore transport of nutrient depleted, warm water. The upwelling/downwelling cycles produce a record that is dominated by variability over a time frame of 1–2 weeks, rather than by a clear seasonal shift in conditions. The seasonality in the monthly mean nutrient data (Fig. 4) is produced by a shift in the frequency and duration of upwelling events that

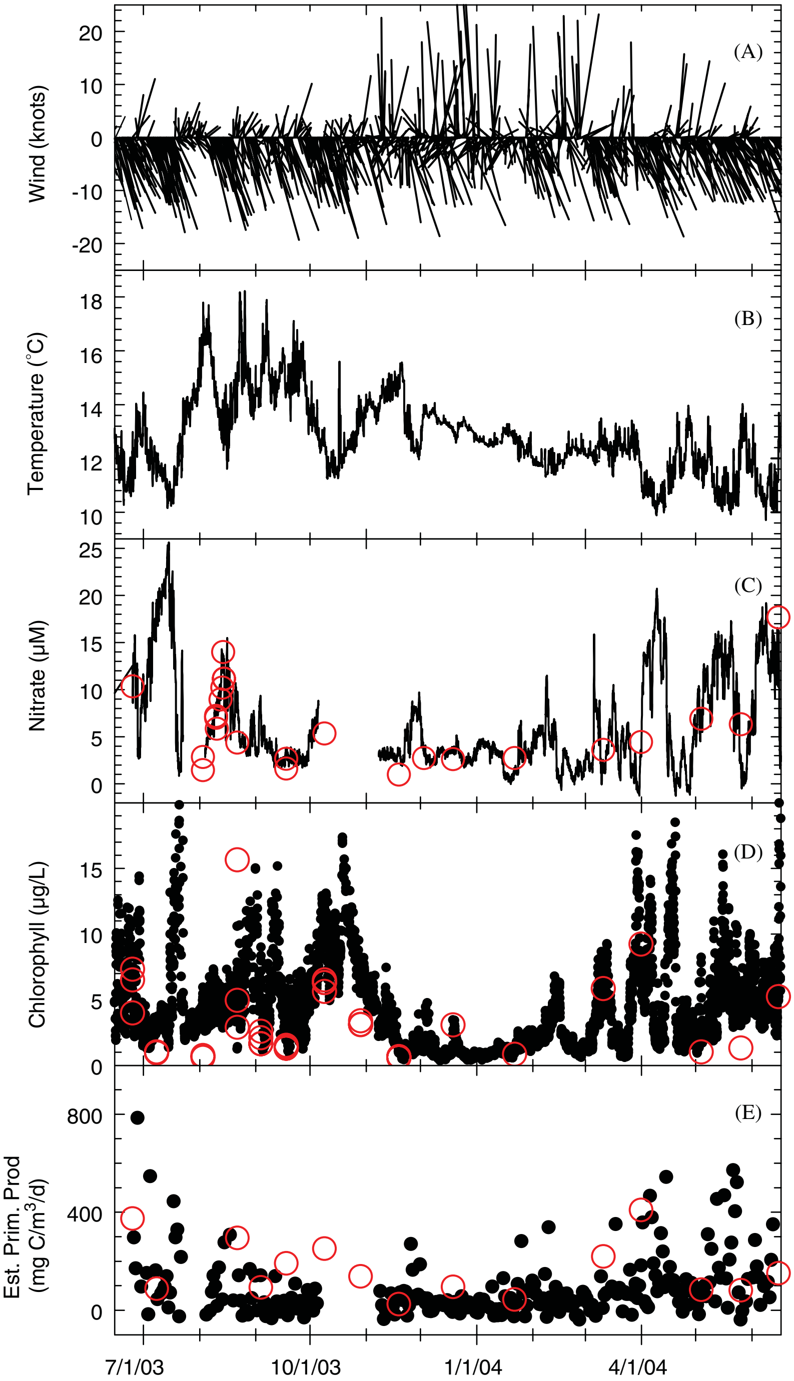

Fig. 2. Observations at the M1 mooring 20 km offshore of Moss Landing on Monterey Bay. Observations were made hourly from 15 June 2003 to 16 June 2004. Wind sticks showing velocity and direction to which wind is moving (A), surface (1 m) water temperature (B), surface nitrate (C), chlorophyll integrated to 10 m (D) and the estimated daily rate of new production (E) demonstrate the system response to episodic events of upwelling produced by wind to the SE. Discrete samples collected at 1 m near the mooring were analyzed for nitrate, chlorophyll and ^{14}C primary production (Pennington and Chavez, 2000) and the results are shown as open red circles.

occur throughout the year, rather than by a continuous presence of upwelling in spring and an absence in the remainder of the year. In that sense, the paradigm that is often used to describe Monterey Bay (Skogsberg, 1936; Skogsberg and Phelps, 1946) as having a spring/summer "upwelling

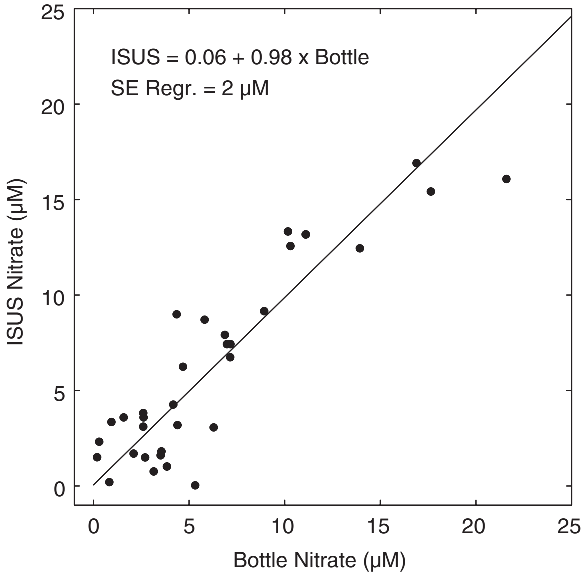

Fig. 3. Comparison of nitrate concentrations determined with moored ISUS sensors and values measured by Alpkem continuous flow analyzer in samples collected periodically at the M1 mooring from 2003–June 2004. Solid line was fitted with a Model II regression (Laws, 1997).

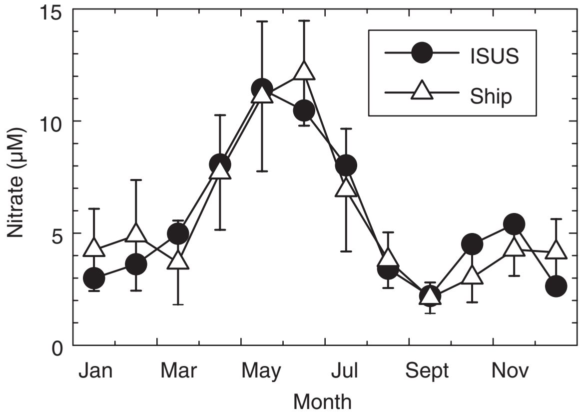

Fig. 4. Monthly mean nitrate concentrations at M1 determined with moored chemical sensors for the period January 2002–October 2004 (circles) and the monthly mean values of observations in samples collected at M1 from 1989 to 2004 and analyzed in shore based laboratories (triangles). Error bars for the shipboard samples are 90% confidence intervals. There are, on average, 1350 hourly samples for each month from the moored sensors and 90% confidence intervals for the mean values are smaller than the size of the symbol.

season”, a summer/fall “oceanic season”, and a winter “Davidson Current season” does not do justice to the high frequency observations (Pennington and Chavez, 2000).

3.2. Diel variability and primary production

Within these multi-week upwelling events, there is significant high frequency variability in the nitrate data. Three segments of the mooring nitrate data from 30 March 2004 to 4 April 2004 (onset of upwelling conditions), 18–23 January 23, 2004 (low wind conditions) and 21–26 May 2004 (relaxation from upwelling) are shown in Fig. 5. A diel cycle in nitrate concentration is clearly visible on the days with elevated nitrate concentrations in spring. This pattern is typical of records at M1 and M2. To emphasize the diel cycle, the nitrate data are high-pass filtered using the Fourier method (Press et al., 1986) to remove frequencies lower than 1 cycle per 33 h. Each segment of nitrate data was quality controlled by eliminating outliers and padding short (<12 h) gaps. The segment was then padded to an even power of 2 data points and the Fourier transform was calculated. The amplitudes of spectral components at frequencies lower than 1 cycle/33 h in the power spectrum were set to zero and the inverse Fourier transform was computed to obtain the high-pass filtered data set. The high-pass filtered nitrate data clearly show daily cycles (Figs. 5(C) and (M)) with concentrations generally decreasing during the daylight (Figs. 5(E) and (O)). The filtered data during winter periods of low nitrate concentration also show a similar, albeit smaller and noisier, signal (Fig. 5(H)).

The diel cycle with nitrate concentrations decreasing during daylight appears to have a biological connection. To explore the relationship to primary production, we calculated the amplitude of each diel cycle. During periods when the mean nitrate concentration is relatively constant, the amplitude is obtained directly from the high-pass filtered data. The mean values of the high-pass filtered nitrate are calculated using 3 h of data from 1300 to 1500 h local (Pacific) standard time and 0400–0600 local time. The diel amplitude is taken as the difference of these values. However, if nitrate concentrations are decreasing, as at the end of an upwelling event (Fig. 5(L)), then the high-pass filtered nitrate concentrations tend to suppress the amplitude of the nitrate change, because the filter removes the day to day decrease in nitrate concentration that may be part of the net community uptake. We, therefore, also calculated the amplitude as the difference in mean (unfiltered) nitrate concentrations over the same time period. The most negative (largest decrease) of the two values is chosen as the

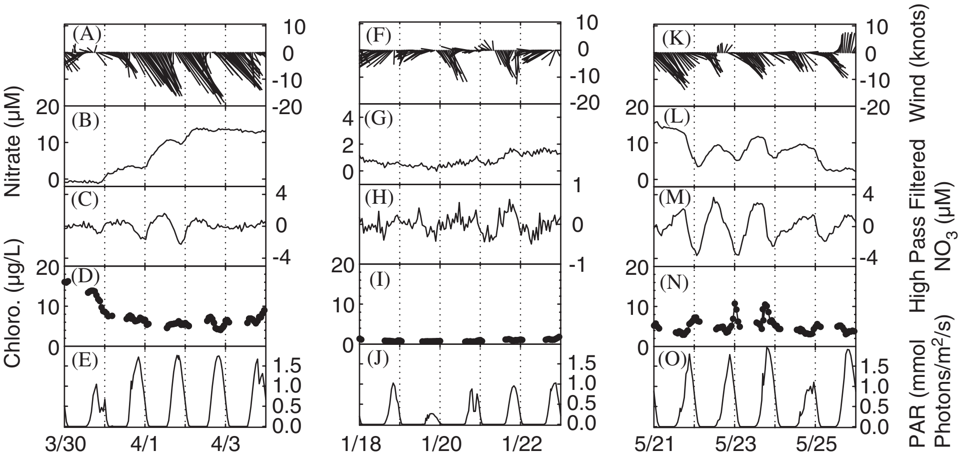

Fig. 5. Wind sticks, surface nitrate, high-pass (33 h) filtered nitrate concentration, chlorophyll integrated to 10 m and photosynthetically available radiation at hourly intervals during 5-day periods in March 2004 (A)–(E), January 2004 (F)–(J) and May 2004 (K)–(O).

amplitude of the diel nitrate cycle. The diel amplitude was extrapolated to a 12 h day and then converted to carbon units with the Redfield ratio (Redfield et al., 1963): $-\Delta NO_3$ (µmol N/L/d) × 6.6 µmol C/µmol N × 12 µg C/µmol C. This product yields an operational estimate of the daily production of new biomass, or new production (mg C m^{-3} d^{-1}). It would not detect production of biomass from recycled fixed nitrogen, primarily ammonia or urea. In the following, we compare this rate of new biomass production with measurements of ^{14}C incorporation into biomass over 24 h periods. The 24 h ^{14}C incubations should yield a rate that approximates net production of biomass (Marra, 2002). This will differ from the rate based on diel nitrate amplitudes because the ^{14}C rate will include biomass production that is supported by all forms of fixed nitrogen. Thus, the ^{14}C measurements should yield somewhat higher rates than do the ISUS sensor based rates.

The diel amplitudes of nitrate concentration observed with the moored sensors are plotted versus the ^{14}C primary production values measured on the same days after transforming the ^{14}C values to daily fixed nitrogen uptake by using the Redfield ratio (Fig. 6(A)). This plot is made with the amplitudes expressed as the nitrate concentration change so that the magnitude of the daily cycles observed on the mooring is apparent. A Model II regression line fitted to all of the data has a slope of 0.73 ± 0.28 (95% CI). This slope is <1, as expected. It suggests that the diel nitrate cycle accounts for a substantial portion (50–100% range, mean 70%) of the fixed nitrogen required to support phytoplankton growth. However, there is also considerable scatter about the regression line. It is likely that much of the scatter is created by physical variability. If so, averaging the new production estimates over a suitable period of time should reduce the scatter. In the following, we compare the new productivity estimates after averaging to monthly or yearly periods with similar averages of ^{14}C primary productivity.

Of the 639 days at M1 with sufficient data to calculate a diel amplitude, 530 days have either no detectable change or a nitrate decrease as shown in Figs. 5(C), (H) and (M). About 17% of the days (109) have diel increases in nitrate during the daytime that are greater than analytical uncertainty of 0.5 µM/d for measurements on a single day. The uncertainty is defined as two times the combined uncertainty of the nitrate values used to calculate the diel amplitude. Several such data points with positive nitrate changes in the daytime are seen in Fig. 6(A). It is unlikely that these nitrate increases at M1 represent days dominated by nitrification or by dark nitrate uptake (Cochlan et al., 1991). More likely, these were simply days on which physical forcing dominated over nitrate uptake. There is a strong, diel cycle of wind during the spring and summer period at M1 (Paduan and Cook, 1997; Service et al., 1998) with maximum wind during the afternoon and low velocities at night, as the land breeze suppresses onshore airflow (e.g., Figs. 5(A) and (K)). Strong daytime winds transport freshly upwelled water from the source near Año Nuevo

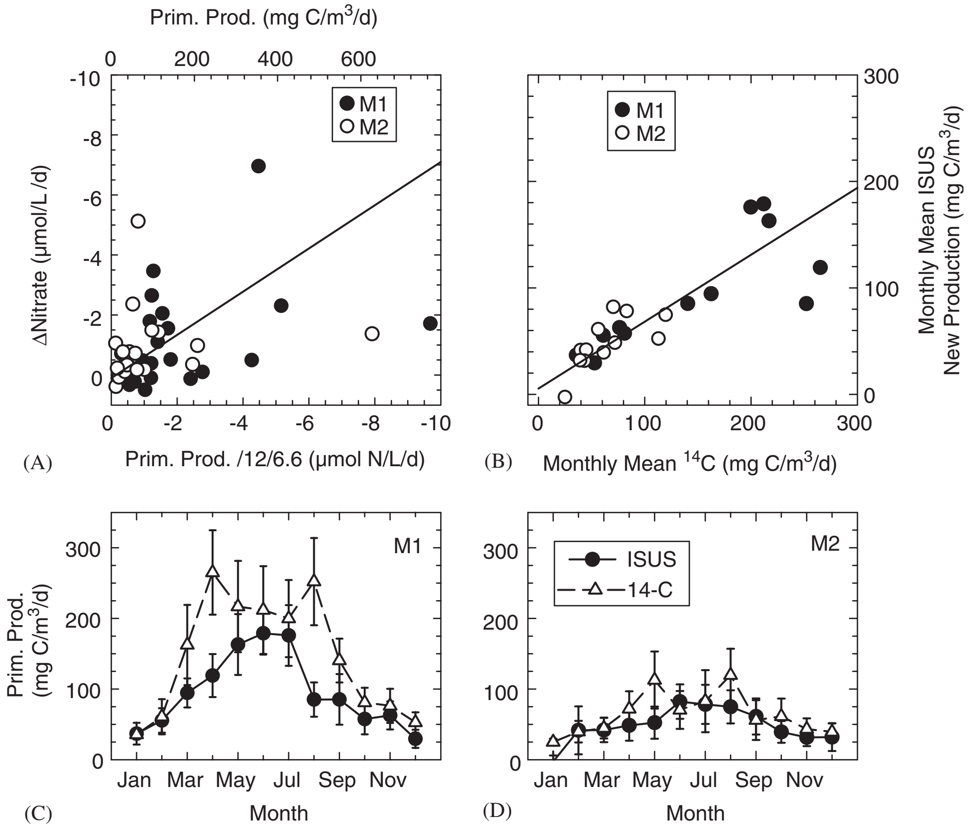

Fig. 6. Comparison of fixed nitrogen required to support daily primary production measured in 24-h incubations using ^{14}C with the diel amplitude of the high-pass filtered nitrate concentration. (A) Diel amplitude of nitrate plotted versus fixed nitrogen required to support ^{14}C primary production measured at M1 (closed circles) and M2 (open circles) moorings. Each comparison is for measurements made on a single day. The Redfield ratio was used to convert ^{14}C primary production to fixed nitrogen requirement. The solid line ($\Delta NO_3 = -0.2[\pm 0.7] + 0.72[\pm 0.3] \times \text{PP-N}$, 95%CI) is fitted by Model II regression. (B) Monthly mean values of new production determined from all diel nitrate amplitudes measured from 2002 to 2004 are plotted versus monthly mean ^{14}C primary production determined from 1989 to 2004 at M1 (closed circles) and M2 (open circles). Solid line is a Model II regression (New Production $= 5[\pm 10] + 0.63[\pm 0.16]$ ^{14}C Primary Production, 95% CI). (C) Monthly mean values of new production determined from all diel nitrate amplitudes measured from 2002 to 2004 (solid circles) and from ^{14}C primary production (open triangles) made from 1989 to 2004 at M1 versus month of year. Error bars are 90% confidence intervals for the data. Panel (D) is the same as (C) at the M2 mooring.

(Fig. 1) past the M1 mooring. If primary production is low, then nitrate concentrations may increase during daytime as nutrient depleted water is replaced by nutrient replete water. Low wind velocities at night can then lead to relaxation of nutrient depleted water back to the mooring, as indicated by the shaded arrows in Fig. 1. This effect of the diel wind cycle is occasionally clear in surface currents mapped with high frequency coastal radars (Paduan and Cook, 1997). M2 is much further offshore, the diel variability in wind is much weaker and, as expected, there are fewer days with daytime nitrate increases. In the analyses reported here, the days with daytime nitrate increases at M1 and M2 that are greater than the analytical uncertainty have been deleted. The impact of eliminating these days is discussed below.

Phytoplankton growth that is based on nitrate is new production (Dugdale and Goering, 1967) and the ratio of new production to primary production based on all forms of fixed nitrogen is the “*f*-ratio” (Eppley and Peterson, 1979). *F*-ratios in Monterey Bay (Kudela and Dugdale, 2000) are typically >0.5 under conditions of high growth, consistent with the slope in Fig. 6(A). The *f*-ratio may decrease to near 0.1 at times in Monterey Bay with lower primary production (Bronk and Ward, 1999), as growth is supported by recycled ammonium ion. At such times of low new production and low biomass accumulation, ^{14}C primary production would be decoupled from nitrate uptake. This must also account for some of the scatter in data at low primary production values (Fig. 6(A)).

It is also clear that a single water parcel does not remain in the vicinity of the mooring over a diel cycle. Daily average surface currents near M1, which are derived from high frequency radars, frequently exceed 20 cm s^{-1} and 24-h trajectories of water parcels may extend more than 20 km (Paduan and Cook, 1997). In order to suppress artifacts due to physical transport, which must contribute to the scatter in Fig. 6(A), we have binned the daily estimates of new production into monthly values after eliminating days with large daytime nitrate increases. The monthly new production values based on diel nitrate cycles are plotted versus month of the year for M1 and M2 in Figs. 6(C) and (D). Over the 2.7 years period with mooring data, there are typically only 4–6 discrete measurements based on ^{14}C in any given month at each mooring due to the ~21 day interval for ship-based sampling. The confidence limits for the ^{14}C data are sufficiently large due to the small number of observations that measurements made only during 2002–2004 do not constrain the values determined from the diel nitrate cycles. The monthly means determined at each mooring using ^{14}C for the period from 1989 to 2004 are, therefore, plotted in Figs. 6(C) and (D). There are, on average, 40 measurements in each month for this extended time period. Primary production values determined by both methods at M1 and M2 show similar patterns over the annual cycle, with the values determined from the diel nitrate cycle about 30% smaller than the ^{14}C monthly averages. The monthly mean new production values are plotted versus the monthly mean ^{14}C primary production values in Fig. 6(B). The monthly mean values of production determined from diel cycles detected with moored sensors and by the ^{14}C method are highly correlated ($R^2 = 0.68$) with a slope of 0.63 ± 0.16 (95% CI). Note, however, that the two monthly measures of primary production span different time periods.

The annual mean values of daily new production that are derived from diel nitrate cycles (2002–2004), from measured ^{14}C values (1989–2004) and from a combined set of $^{15}NO_3^-$ incubations and modeling (1992–1993; Kudela and Chavez, 2000) are shown in Table 1. The annual mean new production values determined from diel nitrate concentration changes at M1 and M2 are 60–90% greater than the annual mean values determined from a model run for 1992–1993, which was calibrated with 82 observations of the uptake rate of isotopically labeled nitrate. Some of this difference may be a reflection of interannual differences in primary production. We show below that the rate of new production is highly correlated with the upwelling index (Bakun, 1975, 1990). The mean value of the upwelling index for both 1992 and 1993 was 21% smaller than the mean for 2002–2004.

There is some uncertainty in the absolute value of the mooring-based new production rate that is created by the occurrence of the days with daytime nitrate increases at M1 and, to a lesser extent, M2. If all of the days with data are used to calculate the annual mean, rather than eliminating the 17% of the days with a daytime nitrate increase greater than analytical uncertainty, then the annual mean productivity estimate at M1 is reduced from 99±11 to 57±13 mg C/m^3/d. We believe that eliminating the days with daytime nitrate increases that are greater than analytical uncertainty results in

Table 1
Annual mean values of new and primary production at M1 and M2

Annual mean value (mg C/m^3/d ± 95% CI)	M1	M2
$\Delta NO_3 \times 6.6$ mol C/mol N × 12 g C/mol C	99±11	55±9
^{15}N new production 1992–1993	63	29
^{14}C primary production 1989–2004	145±21	68±14
Ratio to ^{14}C primary production	0.68±0.12	0.81±0.21

ΔNO_3 values are based on the amplitude of the diel cycle in high-pass filtered nitrate concentration. Error limits are 95% confidence interval. New production values (Kudela and Chavez, 2000) were determined from a model that was calibrated with measurements of the uptake of isotopically labeled nitrate and ammonia and then converted to carbon units using the Redfield ratio. ^{14}C values are average values determined from 313 measurements at M1 and 159 measurements at M2 from 1989–2004.

the more accurate estimate of new production. First, the diel variation in wind at M1 creates a plausible, physical mechanism for producing the increases at M1. Second, the estimates of the *f*-ratio in Table 1, based on sensors at both the M1 and M2 moorings, yield values of 0.68 and 0.81, respectively. Values derived from the slopes in Fig. 6(A) or (B) (0.73 and 0.63, respectively) are not significantly different. These estimates suggest that some 70% of the annual primary production is based on nitrate uptake. The *f*-ratios are reduced by nearly two-fold if all of the diel cycles, including ones with a daytime nitrate increase, are used to calculate the annual new production. Two-fold lower *f*-ratios would require a large amount of the primary production to be based on ammonia, rather than nitrate. However, concentrations of ammonia in Monterey Bay are generally $<0.4\,\mu M$ (Kudela and Dugdale, 2000; FC, unpublished data). Ammonia cannot supply the large amounts of fixed nitrogen that are required to support large rates of primary production (Fig. 6(A)). Large primary production rates will require correspondingly large decreases in the concentration of fixed nitrogen in the Bay and only nitrate appears to be present in sufficient concentration. Thus, we believe that primary production estimates calculated by eliminating the days with daytime nitrate increase are the most accurate.

The daytime drawdown in nitrate concentration will underestimate new production if nitrate is resupplied to the euphotic zone during the day. In this case, the diel amplitude would represent the rate of new production minus the rate of resupply. This may be a significant issue in systems where vertical transport processes dominate nutrient supply. In such systems, the daytime rate could be corrected for resupply by estimating the resupply rate from the nighttime rate of increase. However, lateral advection from the upwelling center at Point Año Nuevo (Fig. 1) dominates nitrate transport at the surface in the region offshore of Monterey Bay. Our calculations presume that we can treat this transport as a homogeneous water mass that flows by the mooring and the daytime drawdown of nitrate is due exclusively to primary production of new biomass. Of course, this cannot be entirely correct on a daily basis, but the monthly averages (e.g. Fig. 6(B)) reported here suggest that the errors are small or must tend to cancel after we eliminate the obvious exceptions when large daytime nitrate increases occur.

3.3. *Regulation of new production*

The estimates of new production that are calculated from the mean of the daily observations for each individual month from 2002 to 2004 are highly correlated with the monthly mean nitrate concentrations (Fig. 7). There is not a significant difference in slopes or intercepts of lines fitted by Model II least-squares (Laws, 1997) to the data sets at M1 or M2 (Fig. 7). The importance of nitrogen in regulating primary production in coastal environments has been demonstrated by experiments with incubated samples (Ryther and Dunstan, 1971; Kudela and Dugdale, 2000). Recent work by our laboratory and others has focused on the role of iron in regulating coastal primary production. Primary production rates along the California and Peru continental margins are often limited by the availability of iron (Hutchins and Bruland, 1998; Hutchins et al., 1998). The M2 mooring is significantly further offshore than M1 (50 versus 20 km), iron concentrations are much lower at M2, and it should be more subject to iron limitation than M1, especially in late summer (Johnson et al., 2001). The lack of a significant difference in the

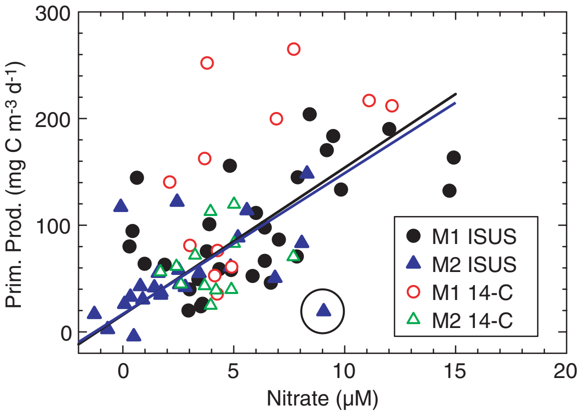

Fig. 7. Monthly mean primary production rates at the M1 and M2 moorings plotted versus mean nitrate concentration. Values of new primary production determined from the amplitude of the diel nitrate cycle for all data in each month from February 2002 to June 2004 are shown as black circles (M1) and blue triangles (M2). The nitrate amplitudes are converted to carbon units with the Redfield ratio. Black and blue lines are Model II regressions fitted to the M1 and M2 data, respectively. Primary production data from ^{14}C incubations determined from 1989 through spring 2004 and averaged by month of year are shown as open red circles (M1) and open green triangles (M2). The October 2002 data point at M2, which is circled, shows the behavior that might be expected if iron limitation is prevalent.

relationship between new production and nitrate concentration at M1 and M2 suggests that decreases in iron concentration at M2 do not act as the major control on primary production. Large-scale iron limitation might also produce a significant number of data points in Fig. 7 that deviated well below the least-square trend lines due to high nitrate, low productivity conditions. Only one of the monthly intervals with ISUS sensor data (October 2002 at M2, which is circled in Fig. 7) has the appearance of falling below the overall trend observed at M1 and M2. Lower annual new production values at M2 occur because the average nitrate concentration is significantly lower than at M1, not necessarily because of greater iron limitation. Iron limitation may be more prevalent further to the south of Monterey Bay, where the continental shelf is narrower and iron concentrations are lower (Bruland et al., 2001; Chase et al., 2005). Long-term deployment of in situ nitrate sensors in that region would provide an interesting test of these hypotheses.

3.4. Inter-annual variations

The main source of nitrate to the euphotic zone in eastern boundary current systems is from upwelled water. As a result, the abundance of nitrate at the M1 and M2 moorings is closely coupled to the rate of upwelling (Fig. 8(A)), where the upwelling rate is

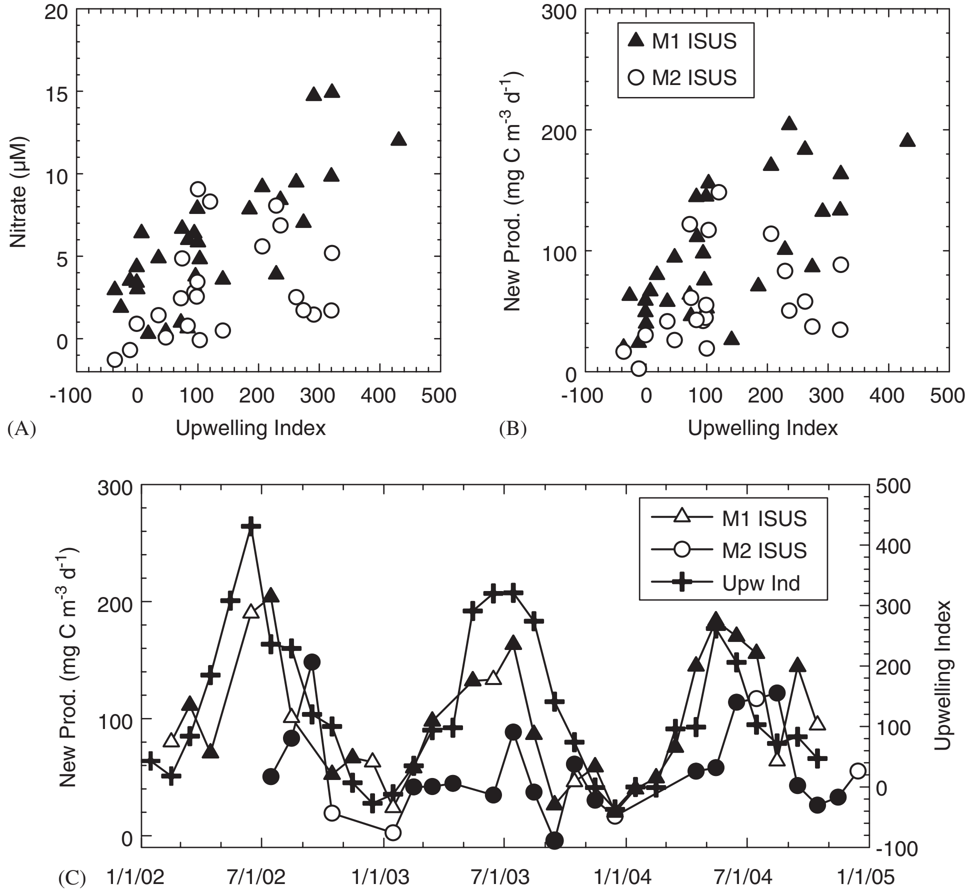

Fig. 8. Relationship between nitrate, primary production and the rate of upwelling. (A) Mean nitrate concentrations determined with ISUS sensors for each month from 2002 to 2004 at the M1 (triangles) and M2 (circles) moorings versus the mean upwelling index for each month at 36°N, 122°W. The units for upwelling index are m^3 of water upwelled/100 m coastline/s. (B) Monthly mean new primary production values at the M1 (triangles) and M2 (circles) moorings versus monthly mean upwelling index. (C) Monthly means of upwelling index (crosses) and new primary production determined with ISUS sensors at M1 (triangles) and M2 (circles) versus time. Open symbols for M1 and M2 represent months where less than 8 days of mooring data are available. Values of the upwelling index (Bakun, 1975, 1990) were downloaded from the website http://www.pfel.noaa.gov.

reported as an upwelling index that is derived from wind stress and coastline orientation (Bakun, 1975, 1990). New production rates, which are correlated with nitrate concentration, are also linked to the rate of upwelling (Fig. 8(B)). Inter-annual variations in the rate of upwelling are the frequently seen. As mentioned above, rates of upwelling in 1992 and 1993 were 21% smaller than the annual means in 2002–2004. Seasonal and interannual changes in the strength and persistence of upwelling favorable winds produce variations in monthly mean productivity values for the same month in different years (Fig. 8(C)). It has been hypothesized that long-term warming will lead to increased upwelling as land warms faster than the sea (Bakun, 1990; Snyder et al., 2003). The results presented here demonstrate a direct means to estimate the impact of such future changes in climate on new production in the ocean.

3.5. New production-based model of biomass

The daily values of nitrate-based new production from June 2003 to 2004 are plotted in Fig. 2(E), along with the ^{14}C values determined during the same period. These estimates are likely the first such high-resolution estimate of the new production cycle in the ocean. New production methods should be capable of predicting the accumulation of phytoplankton biomass (Banse, 2002), but this is difficult because the measurements generally do not have sufficient temporal resolution. To test the capabilities of our high temporal-resolution estimates of new production, biomass was predicted with the equation:

$$B_t = B_{t-1} + \Delta_t \times \mathrm{NPP} - \Delta t \times L \times B_{t-1}, \qquad (1)$$

where B is biomass and NPP is the daily estimate of new production derived from diel cycles of nitrate. L is a rate constant that multiplies biomass to give the rate of loss of biomass. These losses include grazing and physical removal. Δt is the time step for calculations (1 h). Calculated biomass values in units of μM N are converted to chlorophyll units using the Redfield ratio to obtain carbon units and then by assuming a fixed C/chlorophyll ratio (g/g) of 60, typical of Monterey Bay (Johnson et al., 2001). The single adjustable parameter L is fixed at a loss rate constant of 0.4/d, which optimizes the fit. On days where the nitrate concentration increased during the day, the new primary production is estimated from the mean of the two prior days and two following days. Calculations are initiated by

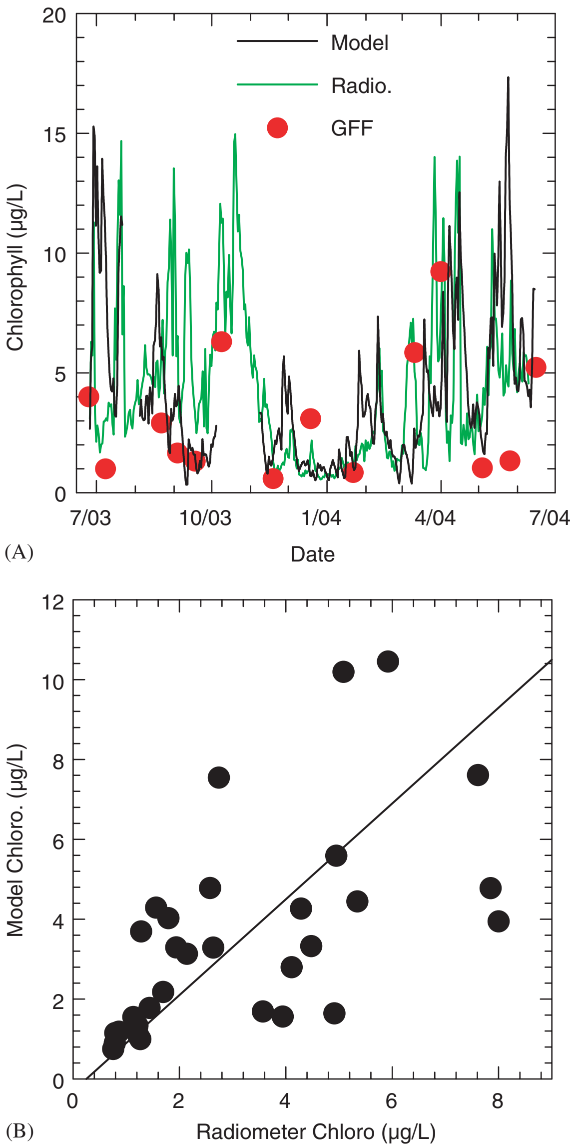

Fig. 9. Predicted values of biomass at the M1 mooring derived from the diel cycles of nitrate. (A) The hourly mean values of chlorophyll derived from the model (Eq. (1)) for the period from 15 June 2003 to 15 June 2004 are plotted versus time as the black line. The green line gives in situ chlorophyll values calculated from observations of light attenuation at 490 nm from the surface to 10 m at the mooring. Extracted chlorophyll values measured in discrete samples collected at the mooring and filtered through Whatman GFF filters are shown as red symbols. (B) The weekly mean values of chlorophyll calculated from the model are plotted versus the weekly mean values of chlorophyll calculated from light attenuation at 490 nm for the period from 8 November 2003 to 14 June 2004. The solid line is the Model II regression equation, Model Chl = −0.4[±1.4] + 1.2[±0.3]Radio Chl, $R^2 = 0.50$.

setting the chlorophyll equal to the value observed on the first hour of each of the three continuous segments of nitrate data in Fig. 2(C). Thereafter, the calculations use no additional information from the observed chlorophyll distribution.

The daily estimates of chlorophyll concentration that have been calculated using Eq. (1) track the chlorophyll concentrations observed with the spectral radiometers on the M1 mooring during most of the year (Fig. 9(A)). Deviations of the model from observations that are shown in Fig. 9(A) may derive from processes not captured in Eq. (1). This includes variability in the grazing rate constant, regeneration of nitrate in situ (nitrification), changes in physical transport or alterations of the carbon to chlorophyll ratio driven by phytoplankton physiology (Johnson et al., 2001). The deviations may also result from sensor drift. There is some evidence that the spectral radiometers were partially fouled during the initial part of this time series, from June to October 2003. During this period, the radiometer estimates of chlorophyll concentration were always several-fold higher than the values of chlorophyll that were determined in shore-based laboratories by fluorescence measurements after extracting chlorophyll from particles retained on Whatman GFF filters (Fig. 9(A)). The mooring was recovered and redployed with recalibrated sensors in late October 2003. From that time until mid-June 2004, there is a very significant correlation between the model and spectral radiometer-based estimates of chlorophyll that are binned to weekly averages to mute high-frequency effects driven by physics (Fig. 9(B)). During this 32-week period, the model explains 50% of the variability in seasurface chlorophyll ($R^2 = 0.50$; Fig. 9(B)). Similar results are generally obtained at M2. If one assumes that much of the remaining 50% of variability is due to physics or other sensor calibration issues, then the bulk of biomass variability is explained by the new production rate. These results require that the major variability in biomass is driven from the bottom up, through changes in new production that are directly coupled to the availability of nitrate.

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