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$\delta^{13}C$ and $\delta^{15}N$ of particulate organic matter in the Santa Barbara Channel: drivers and implications for trophic inference

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ABSTRACT: We investigated the extent to which temporal variation in the stable isotope composition of suspended particulate organic matter (POM) was explained by phytoplankton biomass and production at a southern California (USA) kelp forest and farther offshore in the Santa Barbara Channel. On the reef, $\delta^{13}C_{POM}$ values were positively correlated with chlorophyll *a* concentration and phytoplankton productivity; the latter explained 62% of the variability in $\delta^{13}C_{POM}$. These relationships were weaker offshore, where variation in $\delta^{13}C_{POM}$ was better explained by the abundance of dinoflagellates. As we predicted based on patterns of generally higher phytoplankton biomass and productivity along the shallow shelf, reef $\delta^{13}C_{POM}$ values were typically ^{13}C-enriched relative to values offshore. We used the relationship between chlorophyll *a* and reef $\delta^{13}C_{POM}$ to estimate phytoplankton $\delta^{13}C$ and the contribution of terrestrial C to coastal particulate organic carbon immediately following a rain event. These calculated terrestrial contributions explained 88% of the variability in freshwater runoff (indicated by salinity). $\delta^{15}N_{POM}$ values varied across the year in association with changes in dissolved inorganic N nutrient pools. These results show that trophic studies of coastal marine ecosystems, at least off Santa Barbara, can use inshore POM stable isotope values to represent phytoplankton when freshwater runoff is low. This finding simplifies the use of stable isotopes to infer trophic relationships in southern California kelp forests. Coastal food web studies, particularly those examining kelp contributions, have typically used offshore POM isotope values to represent inshore phytoplankton. Our results show that this assumption may bias results of food web mixing models.

KEY WORDS: Stable isotopes · Kelp forest · Phytoplankton · Suspension feeders · Primary production · Kelp detritus

INTRODUCTION

Suspended particulate organic matter (POM), or seston, is the food source for marine suspension feeders, both benthic and pelagic. Suspension feeders can make up a large proportion of community biomass in coastal habitats including subtidal temperate rocky reefs, where they may comprise >70% of animal biomass (Newell et al. 1982). As primary consumers, suspension feeders are important links to higher trophic levels, including humans, who increasingly culture filter-feeding mussels and other bivalves (Newell 2004, NRC 2010). The feeding ecology of suspension feeders occupies a spectrum of strategies from selective feeding on specific components of POM, such as phytoplankton, to wholesale ingestion of seston (Wildish & Kristmanson 1997). In the coastal ocean, POM may be a complex mixture of particles comprising phytoplankton, marine, freshwater, and terrestrial macrophyte detritus, bacteria, and others (Compiano et al. 1993, Savoye et al. 2003), and teasing apart the contributions of these different components to suspension-feeder diet using tracers such as stable isotopes can be difficult (Page & Lastra 2003, Page et al. 2008).

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A recurrent example of this problem in the literature is detection of the contributions by detritus derived from benthic macrophytes, particularly kelps, to coastal food-web support relative to the contribution of phytoplankton. Kelps are extremely productive in many temperate coastal ecosystems, and often coexist with large populations of subtidal and intertidal suspension feeders. Consequently, many marine ecologists have postulated that kelp detritus is an important source of nutrition for these animals (Nadon & Himmelman 2006, Miller & Page 2012). This has been tested in several geographic areas using natural abundance of stable isotopes: $\delta^{13}C$ as a tracer of kelp and phytoplankton carbon in both POM and suspension-feeder tissues, often in combination with $\delta^{15}N$ as an indicator of trophic level (Miller & Page 2012). Given $\delta^{13}C$ values of phytoplankton and kelp sources, one can estimate the proportion of each end member to a sample of consumer tissue using a 2-source mixing model. Defining the $\delta^{13}C$ value of phytoplankton, however, has been an issue, since POM in areas with abundant kelp has been assumed to be a mixture of kelp detritus particles and phytoplankton. Consequently, most ecologists have relied on phytoplankton samples collected well offshore, far from any presumed kelp influence, to define this carbon source. The key assumption of this approach is that offshore phytoplankton $\delta^{13}C$ values are representative of inshore phytoplankton.

Phytoplankton carbon fractionation is negatively correlated with the ratio of growth, or cellular inorganic carbon demand, to the supply of dissolved inorganic carbon (DIC; Rau et al. 1996, Laws et al. 2002). Therefore, fractionation can be influenced both by growth rate and DIC concentration, with higher growth rate, and consequently higher ratio of DIC demand:supply, leading to lower fractionation rates and enrichment of ^{13}C in phytoplankton. Changes in DIC concentration in seawater, however, may not affect fractionation as much as growth rate, due to carbon concentration mechanisms that allow phytoplankton to sequester CO_2 and maintain high growth rates across a wide range of DIC concentrations (Tortell et al. 2000). Thus, the assumption that offshore phytoplankton $\delta^{13}C$ values are representative of inshore phytoplankton might hold if growth conditions and community composition are similar across the sampling areas, or if phytoplankton is rapidly transported from offshore to kelp forest habitats.

Laboratory culture studies also show evidence of variability in phytoplankton N fractionation with species and growth conditions (Needoba et al. 2003, Altabet 2006). Phytoplankton N fractionation in the ocean, however, on average appears to be relatively constant at ~5‰ (Altabet 2001, 2006, Needoba et al. 2006), with $\delta^{15}N_{POM}$ values varying with relative NO_3^- drawdown reflecting ^{15}N enrichment of the dissolved inorganic nitrogen (DIN) pool through phytoplankton uptake, although there are apparently some taxonomic differences in fractionation (Horn et al. 2011). In the open ocean, $\delta^{15}N_{POM}$ values increase with depth below the euphotic zone due to diagenesis and removal of ^{15}N-depleted NH_4^+ via nitrification and phytoplankton uptake (Altabet 2006).

Most coastal food-web studies using stable isotopic tracers have relied on samples taken within a short time and across a small spatial scale. Isotopes are well suited, in general, to such an approach because consumer tissues provide an inherently time-integrated view of sources, but this integration is limited to the turnover time of consumer tissues, and short-term measurements do not capture variability in the isotope values of primary producers, which can lead to biased estimates of source contributions. Such studies of coastal marine suspension feeders have typically found high contributions of kelp-derived carbon to coastal food webs, including suspension feeders. In a longer-term study, Page et al. (2008) measured monthly variability in POM and giant kelp *Macrocystis pyrifera* stable isotope values ($\delta^{13}C$ and $\delta^{15}N$) over 4 yr at 4 coastal reefs off southern California, USA, concurrent with measurements of *M. pyrifera* biomass and primary production. They found no correlation between biomass or primary production of *M. pyrifera* and stable isotope values of POM across a wide range in variation in kelp abundance. $\delta^{13}C$ values of kelp varied little across time. $\delta^{13}C_{POM}$ values were, in contrast, positively correlated with chlorophyll *a* (chl *a*) concentration, suggesting that phytoplankton were driving variability in POM isotope values.

In this study, we compared the stable isotope composition of POM from a nearshore kelp forest to that offshore in the Santa Barbara Channel. We use concurrent phytoplankton biomass (chl *a* concentration), productivity, nutrient, and particulate organic carbon (POC) data to examine the extent to which phytoplankton community dynamics controls variability of POM stable isotope values inshore versus offshore. Although living *M. pyrifera* also contains chlorophyll, any chlorophyll in kelp detritus will rapidly degrade within the euphotic zone (Nelson 1993). We hypothesized that enriched POM $\delta^{13}C$ values would be associated with elevated phytoplankton abundance and primary production indicative of high growth rates. For offshore samples, we also used quantitative pigment data to examine the relative effect of different

phytoplankton taxonomic groups on POM stable isotope composition. Finally, we predicted that inshore POM, on average, would be significantly enriched in $\delta^{13}C$ compared to offshore POM as a result of differing phytoplankton population dynamics.

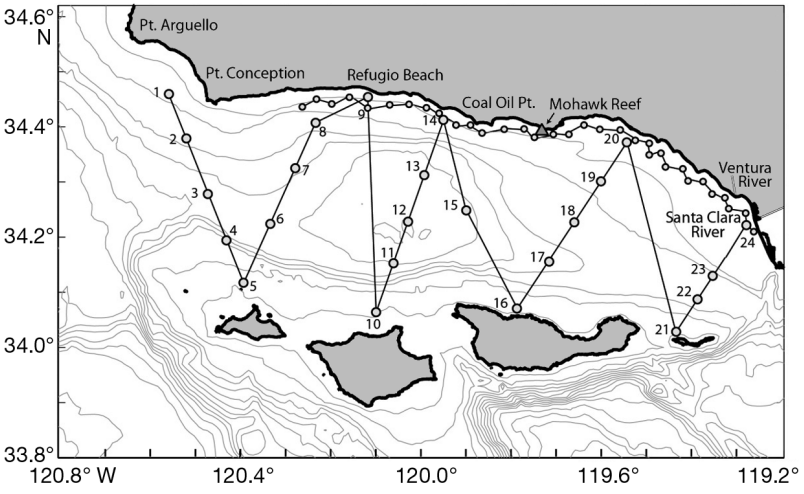

Fig. 1. Study area, showing shoreline, bathymetry (first at 50 m, then at 100 m intervals from 100 m), Santa Barbara Coastal Long-term Ecological Research program (SBC-LTER) cruise tracks (solid lines), location of water sampling stations (large circles), and location of Mohawk Reef (gray triangle). Small circles denote water sampling stations along the E-SCAN cruise line parallel to shore from cruise LTER09

MATERIALS AND METHODS

Study region

The Santa Barbara Channel (SBC) is a region of enhanced phytoplankton biomass and primary productivity within the Southern California Bight (Mantyla et al. 1995). The SBC is 40 km wide by 100 km long, bounded to the north by the California mainland and to the south by the Northern Channel Islands (Fig. 1). Phytoplankton productivity is enhanced in the western SBC due to coastal upwelling combined with the effects of cyclonic circulation on particle retention and vertical nutrient supply (Otero & Siegel 2004, Brzezinski & Washburn 2011). The shallow nearshore fringe of SBC, both along the mainland and Channel Islands and generally <250 m from shore, harbors a patchwork of rocky reefs occupied by forests of the giant kelp *Macrocystis pyrifera*.

Reef POM and primary production

Mohawk Reef, off Santa Barbara, California (34° 23′ 38″ N, 119° 43′ 45″ W), is a shale reef at 5 to 9 m depth that supports a giant kelp forest. We measured POM characteristics and phytoplankton primary production approximately monthly from May 2007 through September 2008 at the offshore edge of the forest, ~150 m from shore. Phytoplankton production was measured using *in situ* ^{13}C-bicarbonate tracer incubations according to the methods of Shipe & Brzezinski (2003). Briefly, a pair of 500 ml polycarbonate light and dark bottles was filled with water collected at 5 depths (1, 2, 3, 4, 6 m) using an 8 l Go-Flo bottle (General Oceanics). Following addition of 0.5 ml of 0.167 mol l^{-1} $H^{13}CO_3^-$ (99.9 atom%), experimental bottles were incubated for ~24 h on a moored line at the collection depths, placed in a dark cooler upon collection, and filtered through pre-combusted (450°C for 2 h) glass fiber filters (0.77 µm nominal pore size) upon return to the laboratory. ^{13}C atom percentage of the particulate matter was measured using a Thermo Finnigan Delta-Plus Advantage isotope mass spectrometer coupled with a Costech EAS elemental analyzer in the UCSB Marine Science Institute Analytical Laboratory. Carbon fixation in the incubation bottles was calculated as:

$$POC_{new} = \frac{(A\%_{sam} - A\%_{nat})}{(A\%_{enr} - A\%_{sam})} \times POC_0 \quad (1)$$

where $A\%_{sam}$ is atom percent ^{13}C measured on the filtered sample after incubation, $A\%_{nat}$ is the average natural abundance of ^{13}C in suspended POC (1.112%, Fernandez et al. 2005), and $A\%_{enr}$ is the atom percent ^{13}C of the labeled substrate. POC_0 is the pre-incubation concentration of POC (µmol C l^{-1}). Production was corrected for dark uptake, including any that occurred between collection and filtration, and integrated through the water column (to 6 m depth). The 24 h carbon tracer uptake best represents net primary production, although high heterotrophic activity during the night may lead to an underestimation of production (Marra 2009).

The concentrations of POC and chl *a* (a proxy for phytoplankton biomass) were measured for each sampling depth. POC concentrations were measured in 630 ml water samples filtered through pre-combusted glass fiber filters and analyzed with a Leeman Labs (Model 440) CHN analyzer. Chl *a* concentration was measured in 200 ml water samples filtered through 0.45 µm, 47 mm cellulose ester Milli-

pore filters and analyzed as described in the next section. POM $\delta^{13}C$ and $\delta^{15}N$ were measured at 1 m depth using 630 ml water samples filtered through pre-combusted (450°C for 5 h) 25 mm glass fiber filters. The filters were stored at −20°C in pre-combusted foil pouches. In the laboratory, filters were thawed, transferred to clean scintillation vials, exposed to dilute HCl fumes to remove carbonates, dried at 65°C, and analyzed using a Thermo Finnigan Delta-Plus Advantage isotope mass spectrometer coupled with a Costech EAS elemental analyzer as above.

Offshore cruises

POM characteristics that included measurements of isotope composition were assessed on 2 cruises in the SBC conducted by the Santa Barbara Coastal Long-term Ecological Research program (SBC-LTER) aboard the RV 'Point Sur' in September 2002 (LTER 05) and October 2003 (LTER08). The cruise track consisted of 8 cross-channel transects beginning at Point Conception and ending near Ventura, California (Fig. 1). Water samples were collected at 25 stations distributed along the cruise track using a CTD/rosette system equipped with 12 l Niskin bottles fitted with vinyl coated springs and a Sea-Bird Electronics 911 CTD. Water samples for inorganic nutrient and chl *a* concentration analysis were collected at all 25 stations at depths of 0, 5, 10, 15, 25, 50, and 75 m; samples for phytoplankton composition analysis using high-performance liquid chromatography (HPLC) were collected at 5 m. Only data from 1 and 5 m samples are presented here.

Samples for inorganic nitrogen analyses were frozen on collection in plastic scintillation vials and analyzed using flow injection techniques on a QuickChem 8000 analyzer (Lachat Instruments Division, Zellweger Analytics) as described by Anderson et al. (2006). Detection limits for NO_3-N and NH_4-N were 0.1 µM. For chl *a* analysis, 125 to 250 ml of seawater were filtered through Millipore HAWP 45 mm cellulose filters, which were immediately frozen at −20°C. Just prior to analysis, the filters were extracted in 90% acetone for 24 h at −20°C. The fluorescence of each extract was measured with and without acidification to determine chl *a* concentrations on a Turner Designs 10AU digital fluorometer that had been calibrated with pure chl *a* (SIGMA Chemical). Analytical precision for the chl *a* determinations was better than 5%. Productivity was measured at 5 m at all stations using ^{14}C-bicarbonate tracer according to the methods of Anderson et al. (2006) as described by Brzezinski & Washburn (2011). POM $\delta^{13}C$ and $\delta^{15}N$ values were measured at 1 and 5 m depth for LTER08 and at 1 m depth for LTER05 at all stations; samples were handled and analyzed as described above.

Phytoplankton community composition: pigment analysis

Phytoplankton pigment concentrations were analyzed by HPLC in the Center for Hydro-Optics and Remote Sensing (CHORS) laboratory at San Diego State University using methods of Bidigare et al. (2002). After filtration of ~1 l surface water onto 0.7 µm Whatman GF/F 25 mm glass fiber filters, each sample was frozen in liquid nitrogen. The filters were later extracted in 4 ml of 100% acetone containing an internal pigment standard (canthaxanthin) to correct for volumetric changes during extraction. An ODS-2 C18 column with a 3-solvent gradient system and a ThermoQuest UV6000 scanning diode array absorption detector were used to separate and quantify pigments in each extract. Chlorophyll degradation products were detected and quantified with a ThermoQuest FL3000 scanning fluorescence detector. All system calibrations were performed using pigment standards from Sigma Chemical and DHI, Institute of Water and Environment, Denmark. Recently it has come to light that HPLC pigment analyses done in this CHORS laboratory did not meet quality standards (Hooker & Van Heukelem 2011), although other analysis suggests that these data do compare favorably with other concurrent HPLC data (Torrecilla et al. 2011). Therefore, analyses based on these data should be viewed as a preliminary exploration into the role of taxon on the isotope composition of SBC phytoplankton.

Terrestrial carbon contribution to reef POM

To test the utility of the relationship between chl *a*, a proxy for phytoplankton biomass, and POM $\delta^{13}C$ from the Mohawk Reef data to estimate phytoplankton $\delta^{13}C$, we used an independent dataset taken during an alongshore cruise in February 2004, LTER09. The cruise track, designated E-SCAN01, ran roughly west along the coast beginning near the mouths of the Ventura and Santa Clara Rivers extending west towards Point Conception, and included the area just offshore of Mohawk Reef (Fig. 1). This cruise track was designed to capture the spatial extent of plumes from these rivers and coastal streams immediately

following a large rain event, <1 d following peak discharge of the 2 river systems (Warrick et al. 2007). Water samples for inorganic nutrient and chl *a* concentration analysis were collected at 59 stations from a depth of 3 m using a rosette system as described above. We estimated phytoplankton $\delta^{13}C$ from each sample using the chl *a* data and the regression relationship between chl *a* and $\delta^{13}C_{POM}$ at Mohawk Reef (see 'Results'). We used the resulting estimate of $\delta^{13}C_{Phyto}$ as one end member in a simple 2-source mixing model to estimate terrestrial carbon contributions to POC in each sample:

$$F_T = \frac{(\delta^{13}C_{POM} - \delta^{13}C_{Phyto})}{(\delta^{13}C_T - \delta^{13}C_{Phyto})} \quad (2)$$

where $\delta^{13}C_{POM}$ is the C isotope value of the E-SCAN01 POM, $\delta^{13}C_{Phyto}$ is the value of phytoplankton estimated using chl *a* as described above, $\delta^{13}C_T$ is the mean value of riverine POM from this area (−24.6‰, Page et al. 2008), and F_T is the proportional contribution of terrestrially-derived POC to the reef POM pool. We used salinity data from the CTD (Sea-Bird Electronics 911) as an indicator of freshwater runoff to evaluate whether terrestrial contributions to the reef POM pool were correlated with runoff.

Data analysis

We explored relationships between the isotope composition of POM and phytoplankton production and biomass using least squares regression (LSR). To partition the pigment HPLC data from the offshore cruises into taxonomic groupings and quantify their contributions to total biomass, we employed the CHEMTAX approach (Mackey et al. 1996). This technique employs an iterative method of factor analysis to solve the least squares equation given by the inputs of raw HPLC pigment data and diagnostic pigment ratio information for each of the major phytoplankton groups of interest. From this series of optimizations, an estimation of the contribution of each phytoplankton class to the total chlorophyll in the sample is derived. The pigments used in the CHEMTAX and their corresponding taxonomic associations were peridinin (dinoflagellates), fucoxanthin (diatoms), 19′-butanoyloxyfucoxanthin (chrysophytes, some haptophytes), 19′-hexanoyloxyfucoxanthin (haptophytes), prasinoxanthin (prasinophytes), violaxanthin (chlorophytes, including prasinophytes), alloxanthin (cryptophytes), lutein (chlorophytes), zeaxanthin (cyanobacteria), and chl *b* (chlorophytes, prasinophytes); chl *a* and total chlorophyll represented total phytoplankton biomass. Pigment ratios were those used by Anderson et al. (2008) for the SBC. The relationship between isotope composition of POM and CHEMTAX estimates of taxon-specific phytoplankton biomass was evaluated using stepwise multiple regression. Statistical analyses were conducted using JMP (SAS Institute, version 8.0.1).

RESULTS

Reef POM

$\delta^{13}C$ values of POM at Mohawk Reef were positively correlated with chl *a* and POC concentrations (Fig. 2A,B). POC and chl *a* were linearly correlated across the 17 mo sampling period, suggesting that POC was dominated by phytoplankton (Fig. 2C). Further supporting this interpretation was the strong positive correlation between chlorophyll and phytoplankton productivity (LSR, phytoplankton production in mg C m^{-2} d^{-1} = 46.96 + 18.26 × chl *a* in mg m^{-2}, $F_{1,26}$ = 60.8, $p < 0.0001$, $r^2 = 0.71$). Phytoplankton productivity was a better predictor of POM $\delta^{13}C$ than chl *a* or POC, explaining 62% of the variability in $\delta^{13}C$; the hyperbolic relationship between POM $\delta^{13}C$ and POM reached an asymptote at ca. −18‰ (Fig. 2D). Phytoplankton productivity at Mohawk Reef peaked during the spring and autumn blooms, with spring bloom productivity rates 2 to 3 times higher than autumn blooms (Fig. 3A). POM $\delta^{13}C$ at Mohawk Reef also peaked during the spring and autumn blooms, but POM $\delta^{13}C$ values for the blooms were similar, reflecting the saturating relationship between productivity and $\delta^{13}C$ (Fig. 2D). POC:chl *a* ratios averaged 116.3 (± 18 SE) and ranged from 45 to 488. POC:chl *a* was lowest during spring and autumn, when phytoplankton blooms were prevalent (Fig. 3B). POM $\delta^{13}C$ was negatively correlated with POC:chl *a* (Fig. 4A), further suggesting that phytoplankton were the drivers of enriched POM $\delta^{13}C$ values. This negative relationship was strengthened by a single high POC:chl *a* value collected on 29 January 2008, 4 d following a rain event.

No trends were apparent between $\delta^{15}N_{POM}$ values and phytoplankton parameters chl *a*, POC, particulate organic nitrogen (PON), or productivity rates; all of these relationships exhibited a pattern of higher variability in $\delta^{15}N_{POM}$ at low values of the phytoplankton parameters (Fig. 4B). There was a weak, but significant, negative correlation between POM $\delta^{15}N$ and total DIN concentration (LSR, $F_{1,25}$ = 5.01, $p = 0.03$, $r^2 = 0.17$) and with both NO_x-N and NH_4-N

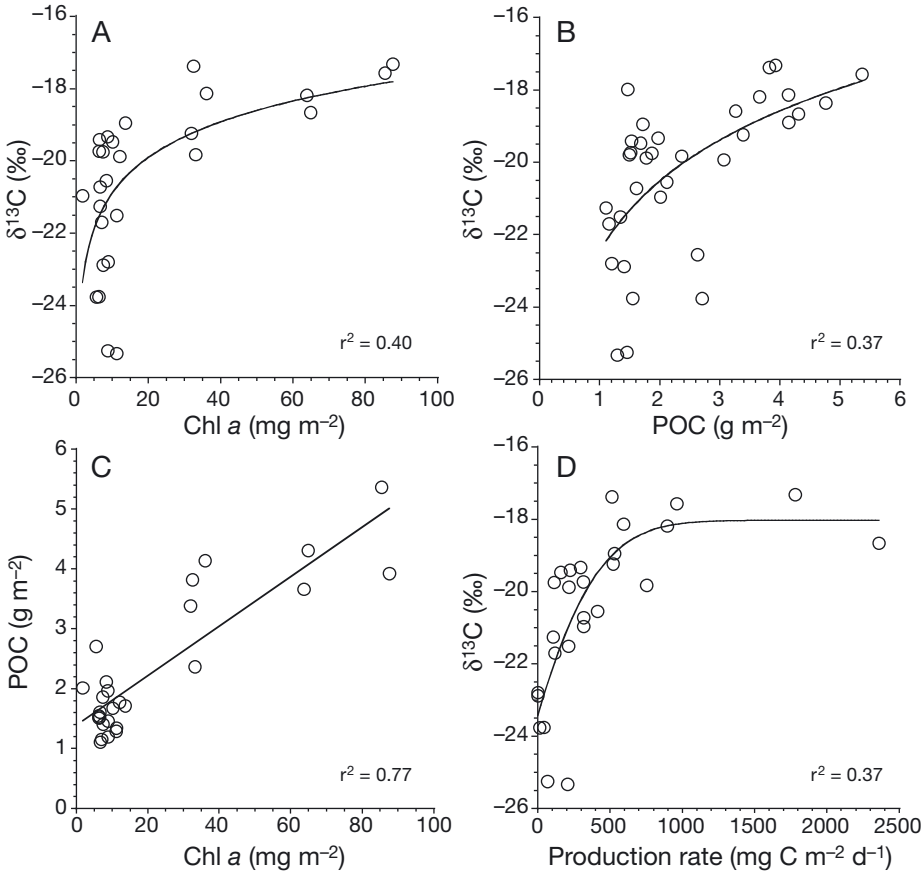

Fig. 2. Relationships between particulate organic matter (POM) characteristics at Mohawk Reef from monthly sampling from May 2007 to September 2008. Chlorophyll *a*, particulate organic carbon (POC), and phytoplankton production are integrated through the 6 m water column. Least squares regression hypothesis test results (except for D) and curve fits are: (A) $F_{1,25}$ = 15.7, p < 0.001, $y = -24.16 + 3.27 \times \log(x)$, (B) $F_{1,25}$ = 20.7, p = 0.0001, $y = -22.46 + 6.44 \times \log(x)$, (C) $F_{1,26}$ = 81.9, p < 0.0001, and (D) Gaussian fit

concentrations. POM $\delta^{15}N$ values showed a positive relationship with the percent of total DIN consisting of NH_4-N (LSR, $F_{1,25}$ = 9.29, p = 0.01, r^2 = 0.42), which was significantly strengthened by lagging POM $\delta^{15}N$ by 1 mo (LSR, $F_{1,25}$ = 20.22, p = 0.001, r^2 = 0.63). POM $\delta^{15}N$ values were also positively correlated with temperature (LSR, $F_{1,25}$ = 8.84, p = 0.01, r^2 = 0.27); temperature was negatively correlated with NO_x-N concentration (LSR, $F_{1,26}$ = 10.3, p = 0.003, r^2 = 0.29). POM $\delta^{15}N$ values peaked in summer to autumn during the 17 mo of the study, along with the percent of total dissolved N that was ammonium (Fig. 5).

Offshore POM

Similar to results at Mohawk Reef, offshore POM $\delta^{13}C$ was positively correlated with chl *a* concentrations and POC, and POC and chl *a* were linearly correlated (Fig. 6A–C). Primary productivity rate was also positively correlated with POM $\delta^{13}C$, but the relationship varied between the 2 cruises (Fig. 6D).

Because isotope studies evaluating the phytoplankton contribution to food webs often sample POM from various distances offshore to obtain a phytoplankton source value uncontaminated by macroalgal detritus, we evaluated whether $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ values varied with distance from shore for the offshore samples. The cruise stations closest to the California mainland were ~1 km offshore and distance increased until the cruise track crossed the middle of the SBC; stations past that point were closer to the Channel Islands than to the mainland. We measured both distance from the mainland and distance to the nearest shoreline for each station. POM $\delta^{13}C$ showed no significant relationship with distance from the nearest shoreline, but a weak negative correlation with distance from the mainland (LSR, $F_{1,74}$ = 3.61, p = 0.06, r^2 = 0.1). POM $\delta^{15}N$ was not correlated to distance from the mainland, but was

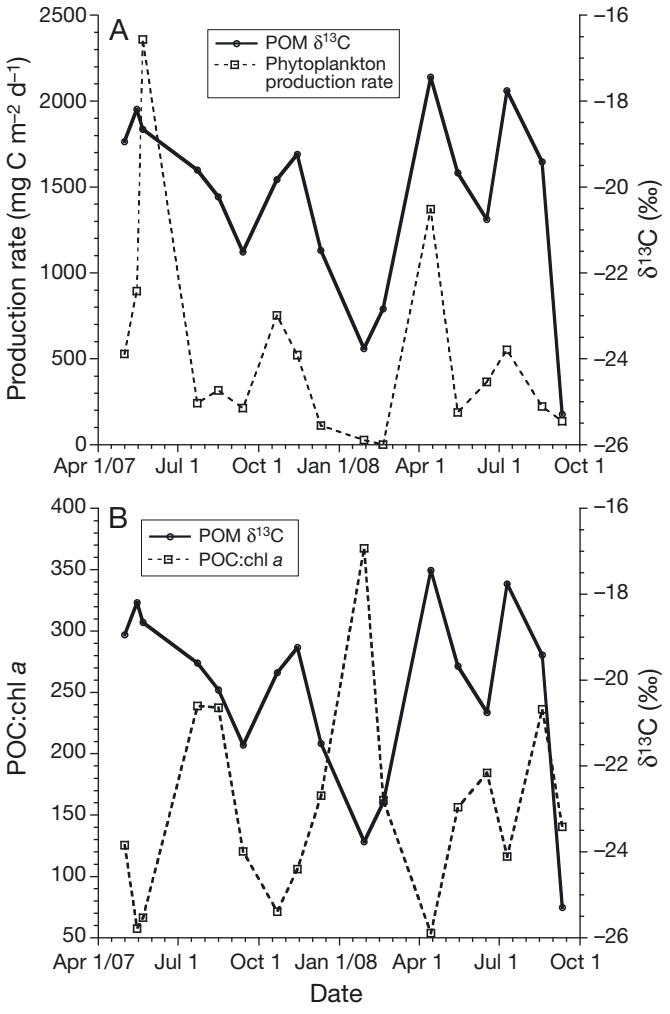

Fig. 3. Time series of particulate organic matter (POM) $\delta^{13}C$ with (A) depth-integrated phytoplankton production, and (B) particulate organic carbon (POC):chlorophyll *a* ratios (weight:weight) at Mohawk Reef

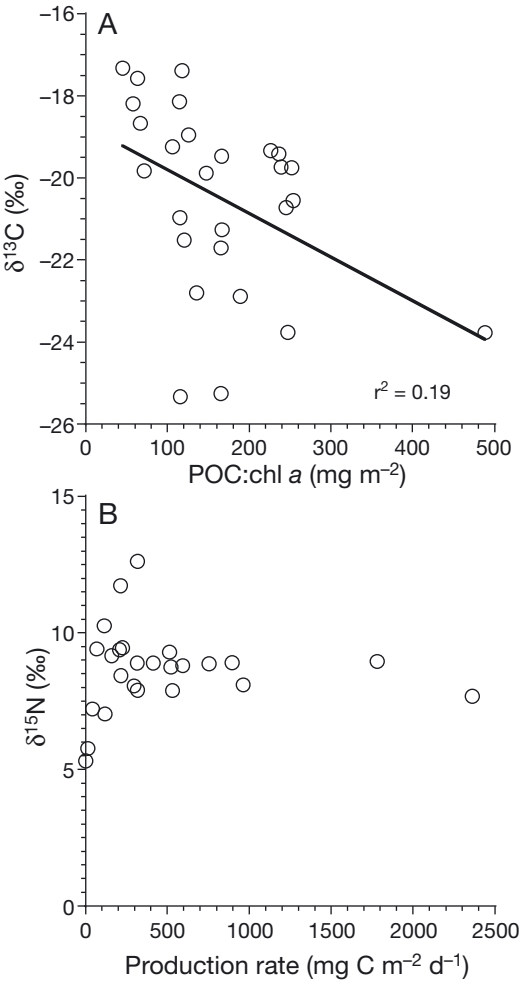

Fig. 4. Relationships (A) between particulate organic carbon (POC):chlorophyll *a* (weight:weight) and particulate organic matter (POM) $\delta^{13}C$ and (B) between POM $\delta^{15}N$ and phytoplankton production, both integrated through the 6 m water column at Mohawk Reef from monthly sampling from May 2007 to September 2008. For (A): least squares regression, $F_{1,24} = 5.74$, p = 0.02

negatively correlated with distance from the nearest shoreline (LSR, $F_{1,74} = 4.80$, p = 0.03, $r^2 = 0.07$), suggesting that mid-channel POM $\delta^{15}N$ values were least enriched. When the 2 cruises were examined separately, LTER08 had a stronger negative relationship between distance from the mainland and POM $\delta^{13}C$ (Fig. 7, LSR, $F_{1,49} = 8.04$, p = 0.01, $r^2 = 0.14$), while there was no significant correlation for LTER05.

As was the case at Mohawk Reef, offshore POM $\delta^{15}N$ values were not correlated with chl *a*, POC, PON, or productivity rates, and all these relationships again exhibited a pattern of higher variability in POM $\delta^{15}N$ at low values of the phytoplankton parameters (e.g. Fig. 4B). Because this pattern was apparent in both the coastal and offshore data, the cause does not appear to have been greater relative to contributions of terrestrial and other sources of organic matter at times of low POM abundance. Unlike the case at Mohawk Reef, there was no correlation between POM $\delta^{15}N$ values and DIN, nor with NO_x-N or NH_4-N concentrations. As at Mohawk Reef, however, offshore POM $\delta^{15}N$ values were positively correlated with the percent of total dissolved N that was ammonium (LSR, $F_{1,74} = 12.1$, p = 0.001, $r^2 = 0.14$). In contrast to the Mohawk Reef data, offshore POM $\delta^{15}N$ values were not correlated with temperature, although the temperature range was similar to that at Mohawk Reef (~13 to 18°C). As with the inshore data, temperature was strongly negatively correlated with (nitrate + nitrite) concentration; a least-squares fit to a fourth-order polynomial between nitrate + nitrite (µmol l^{-1}) and temperature (T,°C) was (nitrate + nitrite) =

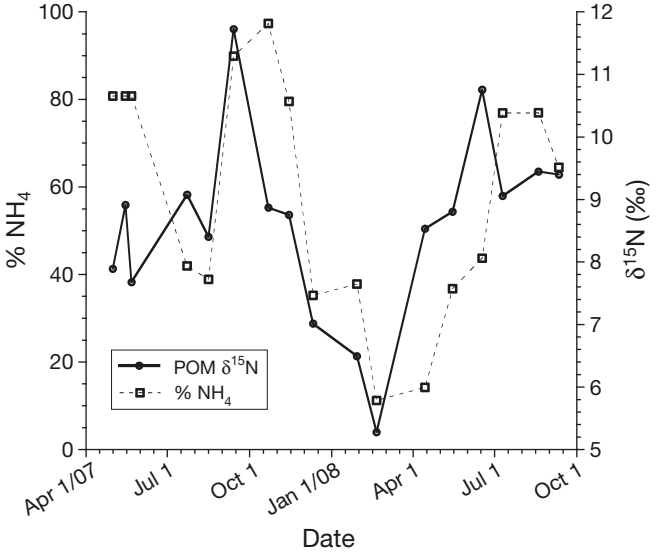

Fig. 5. Time series of particulate organic matter (POM) δ^{15}N and % of dissolved N that is ammonium at Mohawk Reef

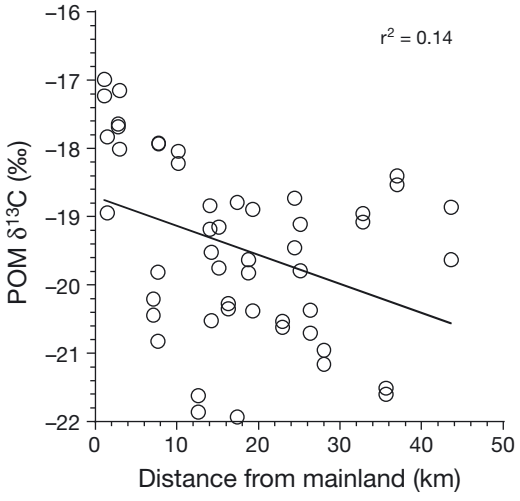

Fig. 7. Relationship between particulate organic matter (POM) δ^{13}C and distance from the mainland for cruise LTER08. $F_{1,49}$ = 8.04, p = 0.007

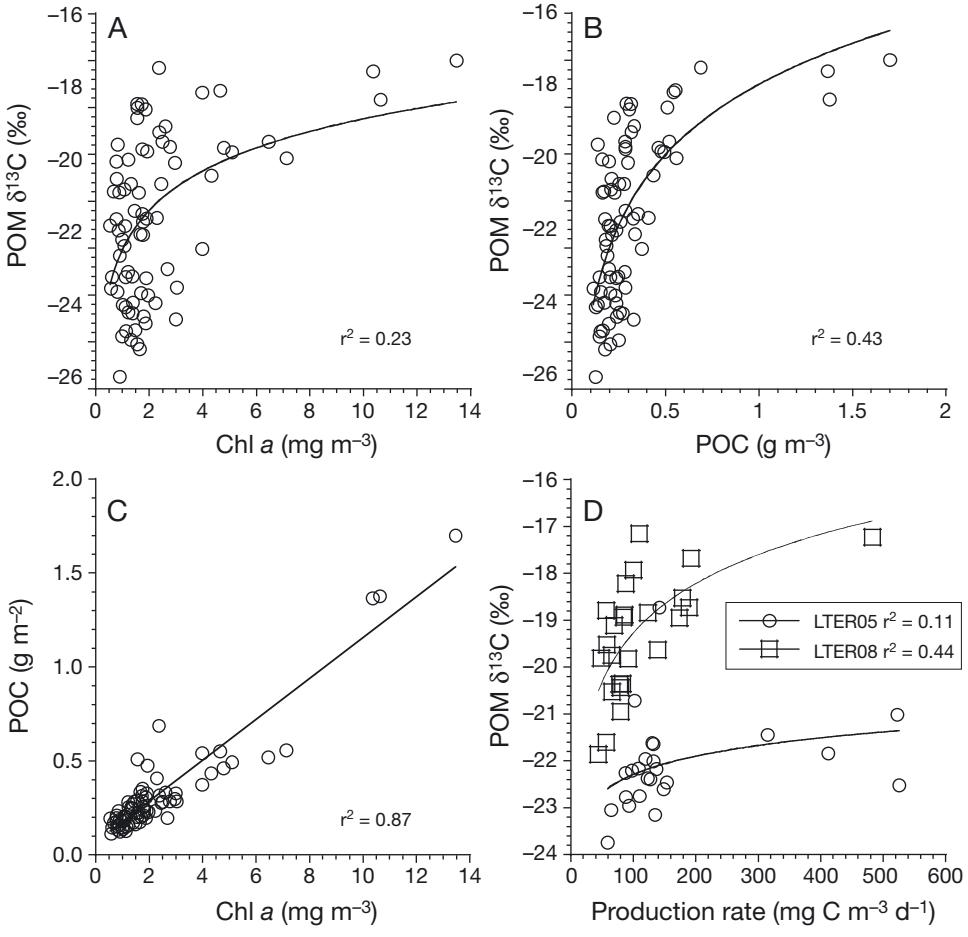

Fig. 6. Relationships between particulate organic matter (POM) characteristics in offshore cruise data. Curve fits are logarithmic except for (C): (A) $y = -21.04 + 2.79 \times \log(x)$, p < 0.0001, (B) $y = -17.51 + 4.96 \times \log(x)$, p < 0.0001, (C) linear $y = 0.07 + 0.11 \times (x)$, p < 0.0001, and (D) cruise LTER05: $y = -24.90 + 0.57 \times \log(x)$, p < 0.0001, cruise LTER08: $y = -26.28 + 1.52 \times \log(x)$, p < 0.0001. POC: particulate organic carbon

$7.726 - 0.447(T) + 0.305(T - 16.3997)^2 - 0.0636(T - 16.3997)^3 - 0.0053(T - 16.3997)^4$ ($F_{4,74}$ = 126.0, p < 0.0001, r^2 = 0.88), a similar relationship to that found by others in the region (McPhee-Shaw et al. 2007), and reflecting the importance of upwelling in the nitrogen supply in this region.

Frequency histograms of POC $\delta^{13}C$ for the Mohawk Reef samples versus the offshore cruises revealed that reef POC $\delta^{13}C$ was skewed to the right compared to the offshore data, which were more normally distributed around the mean value of −20.4‰ (Fig. 8). Although the mean value of the Mohawk Reef POC $\delta^{13}C$ was similar to that of the offshore data at −20.5‰, 59.4% of the POC at Mohawk Reef was ≥ −20‰, compared to 29.6% of the offshore POC (Fig. 8).

Pigment analysis

The CHEMTAX analysis of offshore pigment data revealed that dinoflagellates were the most abundant group of phytoplankton in the offshore samples, making up 27.2 ± 0.03% (mean ± SE) of total chlorophyll, closely followed by diatoms at mean 21.6 ± 0.02%. Prasinophytes (11.3 ± 0.01%), haptophytes (10.1 ± 0.01%), and chrysophytes (11.7 ± 0.01%) were approximately equal in abundance, while cryptophytes (7.4 ± 0.01%) and chlorophytes (2.1 ± 0.003%) were less abundant. Stepwise regression on log-transformed chlorophyll of all taxonomic groups showed that dinoflagellate abundance explained the largest portion of variation in offshore POM $\delta^{13}C$ values ($p < 0.0001$, $r^2 = 0.65$). Adding other groups to the model explained incrementally less variation; the second most explanatory group added was haptophytes ($p < 0.0001$, cumulative $r^2 = 0.73$), and the third was diatoms ($p = 0.01$, cumulative $r^2 = 0.78$). These results were consistently identical when criteria for entering the regression model were varied between minimum Bayesian information criterion (BIC), Akaike information criterion (AIC), or threshold p value. When examined separately, the relationship of dinoflagellate biomass to POM $\delta^{13}C$ values was strongly positive (LSR, $F_{1,47}$ = 86.2, $p < 0.0001$, r^2 = 0.65). CHEMTAX abundances of any taxon did not significantly relate to POM $\delta^{15}N$ values.

Terrestrial contributions to coastal POM

Terrestrially derived organic matter composed 32.8% (± 3.2% SE) of coastal POM off the Santa Barbara coast following the heavy freshwater runoff event sampled in February 2004 on cruise LTER09 along the E-SCAN01 line (Fig. 1), as estimated using the mixing model and chlorophyll-derived value for phytoplankton $\delta^{13}C$. Of the variation in salinity, an indicator of freshwater runoff, 89% was explained by the calculated terrestrial contribution (% terrestrial POC, Fig. 9).

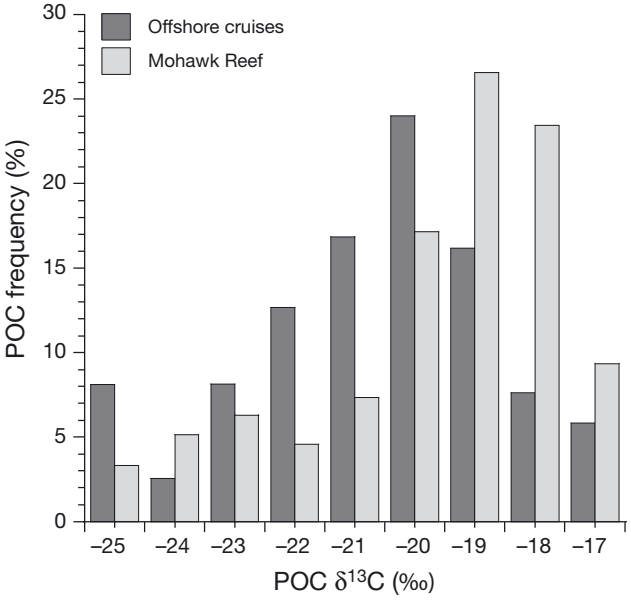

Fig. 8. Frequency distribution of $\delta^{13}C$ values for particulate organic carbon (POC) from Mohawk Reef versus offshore cruises. Distributions are significantly different (chi-squared test, $p < 0.00001$)

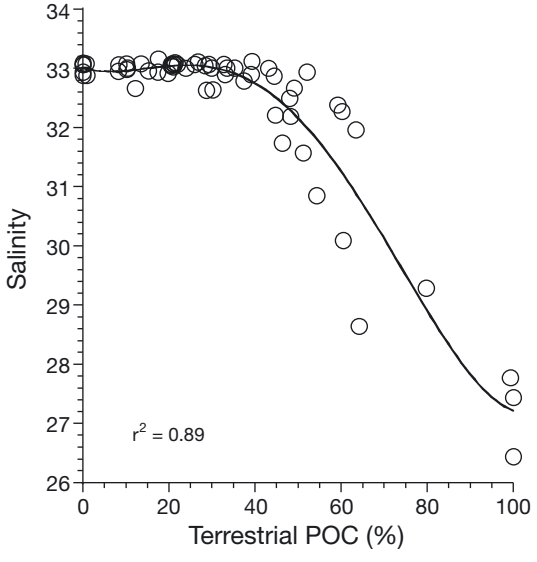

Fig. 9. Salinity, an indicator of freshwater runoff, versus the calculated terrestrial particulate organic carbon (POC) contribution (%total organic carbon) for coastal Santa Barbara Channel sampled on cruise track E-SCAN01. Least-squares fit to 3rd-order polynomial, $F_{3,58}$ = 138.9, $p < 0.0001$, $r^2 = 0.88$

DISCUSSION

At Mohawk Reef, the correlations between POM $\delta^{13}C$ and phytoplankton biomass (chl *a* concentration) and phytoplankton productivity suggest that most variability in POM $\delta^{13}C$ near shore is driven by phytoplankton population dynamics. Further supporting this interpretation is the tight linear relationship of both POC and productivity with chl *a* concentration, which indicates that most suspended POC on the reef was living phytoplankton. Chlorophyll in detritus degrades rapidly in the euphotic zone (Nelson 1993). Under high irradiance conditions such as those typical of SBC surface waters, chlorophyll in phytoplankton detritus degraded quickly and largely disappeared by 4 h (Mayer et al. 2009). Furthermore, kelp detritus would not contribute to water column productivity, which was strongly correlated with chl *a* concentration.

Parsons et al. (1961) reported a range in the ratio of POC:chl *a* (weight:weight) of 20 to 200 in phytoplankton. POC:chl *a* values at Mohawk Reef were largely within that range, except for some higher values in winter and autumn (Fig. 3B). If additions of ^{13}C-enriched kelp detritus were driving enrichment of POM $\delta^{13}C$, as many studies have suggested (reviewed by Miller & Page 2012), we would expect POM $\delta^{13}C$ to be positively correlated with POC:chl *a*, since detritus is characterized by high C:chl ratios (Cifuentes et al. 1988, Mayer et al. 2009). Instead, the correlation between these variables was negative, suggesting that phytoplankton blooms were the cause of enriched POM $\delta^{13}C$ values (Fig. 4). In our study area, instead, it is likely that depleted POM $\delta^{13}C$ values are driven at least at times by terrestrial input, as indicated by the high value of POC:chl *a* observed after a rain event. Terrestrially-derived POM is likely to have high C:chl ratios (Cifuentes et al. 1988). Others have used POC:chl *a* ratios to infer detritus abundance. For example, the *y*-intercept of the regression of chl *a* and POC abundance can be taken as an approximate estimate of detrital C abundance in low-chlorophyll samples (Nelson et al. 1989). Our data from Mohawk Reef suggest that depth-integrated detrital POC was ~1.4 g m^{-2}, 1.9 µmol l^{-1} within the 6 m water column, which corresponds to 5.6% of average POC concentration. This value is comparable to the rather low value found by Nelson et al. (1989) in the diatom-dominated Southern Ocean. Correspondingly low C:chl ratios have been found in other nearshore waters (Schaefer & Lewin 1984, Wienke & Cloern 1987, Putland & Iverson 2007), and in one of the few studies examining spatial variability in C:chl values, Chang et al. (2003) found lower values along the coast of the China Sea compared to offshore.

The Southern California coast in the Santa Barbara area has a relatively dry climate with episodic rains in winter, which limits terrestrial carbon inputs (Page et al. 2008). Abundance and productivity of macroalgae, however, particularly the giant kelp *Macrocystis pyrifera*, is high at Mohawk Reef and other sites with hard substrate along the coast (Reed et al. 2008, Miller et al. 2011). Many analyses of temperate coastal food webs have interpreted enriched POM $\delta^{13}C$ values as reflecting kelp carbon inputs into a mixture including depleted phytoplankton (Nadon & Himmelman 2006, Miller & Page 2012). Our results show that this view can be incorrect, and that enriched POM $\delta^{13}C$ values near the coast can reflect variability in phytoplankton values, possibly driven by high phytoplankton growth rates. These results strongly indicate that single-point measurements of POM $\delta^{13}C$ are not sufficient for inferring trophic contributions of kelp or phytoplankton to coastal food webs.

Kelp carbon is certainly produced in abundance along the California coast; if it is not evident in the POC pool, where is it going? A relatively small fraction of *Macrocystis pyrifera* biomass is consumed in the forest; estimates range from 3 to 6% (Gerard 1976, Newell et al. 1982). Large amounts of kelp are removed by wave action, after which it can drift for considerable distances (Hobday 2000) and can either be deposited on shore or sink into deep water. In both of these food-limited habitats, invertebrates rapidly consume kelp (Griffiths & Stentondozey 1981, Vetter 1995, Lastra et al. 2008), and microbes remineralize buried kelp biomass (Dugan et al. 2011). Quantifying these alternative fates of kelp primary production is needed if we are to estimate the potential contribution of kelp carbon to POC pools. Most kelp carbon may be remineralized in the benthic or intertidal zone as large fragments of biomass, rather than broken down into small, suspended particles.

Offshore POC (cruise data) was often depleted in ^{13}C compared with reef POC, indicating that the use of offshore $\delta^{13}C_{POM}$ values as a proxy for inshore phytoplankton $\delta^{13}C$ values in mixing models can introduce appreciable error in estimates of the relative contributions of phytoplankton and kelp detritus to reef POM. As an example, if we assume a typical average $\delta^{13}C$ value for kelp at –13‰ and a reef POM $\delta^{13}C$ of –18‰, using an offshore phytoplankton value of –20‰ in a 2-source mixing model results in an estimated kelp contribution to reef POM of 25% (as opposed to 0% if inshore POM values represent

phytoplankton). Reef POM $\delta^{13}C$ ranged from ca. −17 to nearly −26‰ in our study, and reached values as high as −14‰ in a 4 yr study of 4 SBC reefs (Page et al. 2008). Our results strongly suggest that this variability is driven by phytoplankton, and that invoking kelp detritus input as a source of POC to SBC, and likely to temperate coastal ecosystems in general, is unwarranted.

Our offshore cruise data were more limited in temporal scope than the Mohawk Reef data, with samples best representing autumn. This limitation may have contributed to the somewhat more variable relationships between offshore POM $\delta^{13}C$ and chl *a* and phytoplankton productivity. Taxonomic makeup of the phytoplankton communities offshore versus inshore may also have contributed to these differences. Dinoflagellate blooms typically increase in autumn in SBC (Anderson et al. 2008, Goodman et al. 2012); CHEMTAX data showed that dinoflagellates were the most abundant group present in the offshore samples, and dinoflagellate abundance was positively correlated with POM $\delta^{13}C$. Previous studies showing that dinoflagellates were more common in autumn in SBC support these pigment results, and suggest that potential problems in the CHORS HPLC data used in this study (see 'Materials and methods') do not preclude inference about broad taxonomic groups using these data (Torrecilla et al. 2011). Coastal phytoplankton productivity in SBC is generally dominated by diatoms during spring (Goodman et al. 2012), which can become highly ^{13}C-enriched during blooms (Fry & Wainright 1991). A relative lack of diatom blooms during the cruises may have therefore contributed to the variability in the relationship between POM $\delta^{13}C$ and phytoplankton productivity in the offshore samples. Reinforcing this view is the fact that dinoflagellates were more prevalent during LTER05, which showed lower POM $\delta^{13}C$ enrichment with increasing productivity compared with LTER08 (Fig. 7D). Dinoflagellates composed 4.6% of chlorophyll on LTER08, compared to 8.9% for LTER05. Although we do not have data on cyanobacterial abundance for these samples, cyanobacteria may fractionate carbon isotopes to a greater degree than other taxa (Wainright & Fry 1994), and greater abundance of cyanobacteria in the offshore samples may have contributed to the difference in the relationships between chlorophyll, productivity, and POM $\delta^{13}C$ there compared with Mohawk Reef.

The positive relationship between POM $\delta^{13}C$ and phytoplankton biomass and production shown here is not unexpected. Theory and experiments have shown that carbon isotope fractionation by phytoplankton is negatively correlated with the ratio of growth, or cellular inorganic carbon demand, to DIC supply (Rau et al. 1996, Baird et al. 2001, Laws et al. 2002). Therefore, fractionation can be influenced both by growth rate and DIC concentration, with higher growth rate, and consequently higher ratio of DIC demand/supply, leading to lower fractionation rates and enrichment of ^{13}C in phytoplankton. Comparison of laboratory cultures and field samples suggests, furthermore, that *in situ* phytoplankton growth rates can be inferred from $\delta^{13}C$ values (Bidigare et al. 1997), although this relationship can be confounded if changes in growth rate are accompanied by changes in biochemical composition, e.g. cellular lipid content (Laws et al. 2002). Changes in DIC concentration in seawater, however, may not affect fractionation as much as growth rate does, due to the presence of carbon concentration mechanisms (CCM), which are apparently widespread in phytoplankton (e.g. Price & Badger 2002). CCM can allow phytoplankton to sequester CO_2 and maintain high growth rates across a wide range of DIC concentrations, as reflected by results for coastal phytoplankton assemblages dominated by diatoms (Tortell et al. 2000). Nevertheless, across large temperature fluctuations, DIC concentration may affect the relationship between growth rate (and consequently chlorophyll and production) and POM $\delta^{13}C$ (Rau et al. 1992, Wainright & Fry 1994). Thus, the relationships between chlorophyll and production and POM isotope composition demonstrated here should be evaluated independently in different regions.

POM $\delta^{15}N$ at Mohawk Reef varied across the 17 mo of the study by nearly 7‰ (Fig. 6). This corresponds to ~2 to 3 trophic levels of enrichment using an estimate of 2.2 to 3.4‰ per trophic level (DeNiro & Epstein 1981, Vander Zanden & Rasmussen 2001, McCutchan et al. 2003). This level of variability is expected in fast-growing phytoplankton, and suggests that using primary consumers with long tissue turnover times may be a more efficient way to obtain an isotopic baseline for phytoplankton (Cabana & Rasmussen 1996, Post 2002). Since turnover times generally scale with body size, larger primary consumers may provide a better isotopic baseline (Post 2002). The difficulty with this, of course, is choosing consumers that are known to rely wholly on the source of interest, in this case phytoplankton. In the SBC kelp forest study system, this problem is simplified by the fact that kelp, the other putative source of N, has a $\delta^{15}N$ similar to POM (Page et al. 2008). Therefore, large suspension feeders, e.g. bivalves, could be used to define the basal consumer trophic level for food web studies.

POM $\delta^{15}N$ values can become enriched as phytoplankton draw down NO_3^-, and the DIN pool becomes more enriched as it gets smaller (Cifuentes et al. 1988, Altabet 2006). Additionally, phytoplankton fractionation may be lower at high growth rates and low N concentrations (Wada & Hattori 1978). The Mohawk Reef POM $\delta^{15}N$ data are consistent with this dynamic: POM $\delta^{15}N$ was negatively correlated with (nitrate + nitrite) on the reef, but there was no such correlation in the offshore data. In both the reef and offshore data, however, POM $\delta^{15}N$ was positively correlated with the relative abundance of ammonium as a percent of total N. Remineralization of organic matter in sediments may be the main source of NH_4^+ to coastal waters and can provide as much as 50% of primary producers' annual N requirements (Klump & Martens 1983, York et al. 2007) in some regions. Sediment-regenerated NH_4^+ can become ^{15}N-enriched due to nitrification to NO_3^-, which has a large associated fractionation (ε) ranging from +12 to +38‰ (Casciotti et al. 2003, York et al. 2010). Ammonium has been postulated to be an important source of N to the nearshore SBC (Warrick et al. 2005, Fram et al. 2008), particularly in summer (Fram et al. 2008), and is generally preferred by phytoplankton over nitrate (Dortch 1990). The increased POM $\delta^{15}N$ with relative ammonia abundance could be explained by an increase in utilization of regenerated NH_4^+ by phytoplankton, possibly coupled with the lower ε that may occur with nitrogen limitation (York et al. 2007). The positive correlation of POM $\delta^{15}N$ with the relative abundance of ammonium in the offshore samples, although weaker than that inshore, suggests that ammonium may be an important nitrogen source to phytoplankton throughout the channel when dissolved inorganic N is low.

Although sampling a time series of POM and consumer stable isotope composition is a larger investment of resources compared to a 'snapshot' study, these results show that reef POM $\delta^{13}C$ can be used as a proxy for phytoplankton $\delta^{13}C$, if the relationship between POM $\delta^{13}C$ and phytoplankton abundance is supported. Developing such a relationship using data from time periods lacking other sources of interest, such as terrestrial inputs, may allow the use of mixing models to calculate the contribution of such sources to the POM pool. We used the significant relationship between chl *a* and POM $\delta^{13}C$ at Mohawk Reef to predict phytoplankton $\delta^{13}C$ from an independent dataset, and estimated terrestrial carbon inputs to the coastal POM pool off Santa Barbara when an extensive riverine plume was present. Of the variation in salinity, an indicator of freshwater runoff, 89% was explained by the calculated terrestrial POC contributions. This suggests that the phytoplankton end member calculated using chl *a* was reasonable, and that this relationship can be used to estimate phytoplankton $\delta^{13}C$ for coastal food web studies.

CONCLUSIONS

Our results indicate that the POC, and therefore POM, in the coastal waters of the SBC is composed primarily of phytoplankton, and that bloom dynamics and possibly taxonomic composition of the phytoplankton community drive variability in POM $\delta^{13}C$. This pattern suggests that macroalgae such as kelps may not significantly contribute to inshore POM even where they are very abundant, as is the giant kelp *Macrocystis pyrifera* in SBC. This conclusion is supported by previous results that showed no correlation between kelp abundance and POM $\delta^{13}C$ (Page et al. 2008). The assumption that offshore POM $\delta^{13}C$ can be used to represent inshore phytoplankton, which has been often used in coastal marine stable isotope studies (reviewed by Miller & Page 2012), was not supported, and this practice has likely led to widespread overestimation of the contribution of kelp carbon to nearshore ecosystems and particularly to suspension feeders. POM $\delta^{15}N$ also exhibited significant temporal variability both inshore and offshore that is apparently influenced by nitrogen availability. Food web studies can meet the challenge of variability in POM isotope composition by sampling across a time series for $\delta^{13}C$ and by using large suspension feeders to integrate temporal variability in the $\delta^{15}N$ value for basal consumers. For periods of time or areas where other inputs, such as terrestrial inputs, are inferred, relationships between chl *a* and POM $\delta^{13}C$ can be used to estimate phytoplankton $\delta^{13}C$ for use in mixing models. Stable isotopes provide an integrated measure of trophic relationships that is methodologically straightforward and can be used in long-term studies essential to elucidating trophic shifts due to climate change. Our results provide important evidence showing that expensive and technically challenging methods for physically separating phytoplankton from POM to obtain an uncontaminated isotope value for mixing models may not always be needed in coastal marine systems, since POM stable isotope composition can reflect that of phytoplankton quite well. This finding simplifies future use of stable isotopes as tracers of organic matter in kelp forest ecosystems.

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