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Production and partitioning of organic matter during simulated phytoplankton blooms

Michael S. Wetz and Patricia A. Wheeler
College of Oceanic and Atmospheric Sciences, 104 Ocean Administration Building, Oregon State University, Corvallis, Oregon 97331

Abstract

Few studies have examined the partitioning of organic matter in upwelling systems, despite the fact that these systems play a key role in carbon and nitrogen budgets in the ocean. We examined the production and partitioning of phytoplankton-derived organic matter in deck incubations off Oregon during the upwelling season. During exponential growth of the phytoplankton, ≥78% of total accumulated organic matter was in particulate (POM) form. This suggests that dissolved organic matter (DOM) is a small fraction of primary production during the exponential growth of coastal phytoplankton blooms. After nitrate depletion, carbon-rich (C : N ≥ 16) DOM accumulated in incubations dominated by the diatom *Chaetoceros* sp., accounting for 38% (±8.5%) of accumulated total organic carbon (TOC) and 24% (±8%) of accumulated total organic nitrogen (TON). However, in a bloom dominated by the diatom *Leptocylindrus minimus*, a relatively smaller amount of DOM accumulated, accounting for only 15% of accumulated TOC and 7% of accumulated TON. On the basis of measured concentrations of nitrate and accumulated TOC, ~70%–157% more carbon was fixed than would be predicted by Redfield stoichiometry (referred to as ''excess carbon fixation''), with 20%–69% of the excess carbon fixation occurring after nitrate depletion. The accumulation of carbon-rich DOM and excess carbon fixation suggests that nitrate assimilation (i.e., new production) might not equate to net production of POM in coastal upwelling systems.

Coastal upwelling systems are among the most productive marine ecosystems in the world. Although accounting for only 1% of total ocean surface area, coastal upwelling regions account for ≥10% of global new production (Chavez and Toggweiler 1995). New production is defined as primary production that is based on newly available nitrogen (Dugdale and Goering 1967) and is commonly determined from regional observations of nitrate-based primary production, because nitrate is globally the main source of new nitrogen to the euphotic zone. In coastal regions, the fate of new production is thought to be export through sinking of particulate organic matter (POM) or through the accumulation of higher trophic level biomass (e.g., fish production) (Eppley and Peterson 1979; Walsh 1991). However, earlier paradigms are now being revisited, because numerous studies have shown an accumulation of dissolved organic matter (DOM) after phytoplankton blooms and over the course of the growing season in a variety of marine systems (Ittekkot et al. 1981; Bronk et al. 1994; Williams 1995). Additionally, elevated carbon fixation relative to nitrogen assimilation has been observed in the surface ocean (Sambrotto et al. 1993). The fate of this excess fixed carbon is largely unknown. Mechanisms, such as aggregate formation resulting from transparent exopolymer (TEP) production by phytoplankton, are now being elucidated, and these might facilitate rapid export of the excess fixed carbon from the euphotic zone (Engel et al. 2002).

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Until recently, the marine DOM pool has received relatively little attention because of its complexity. There are many sources of DOM in the marine environment, including phytoplankton exudation (Hellebust 1965), grazing (Strom et al. 1997), viral lysis (Bratbak et al. 1990), bacterial degradation of detritus or aggregates (Biddanda 1988; Smith et al. 1992), and terrestrial input (Hill and Wheeler 2002). In most marine systems, including coastal upwelling regions, the relative contribution of the various sources is largely unknown. In addition to having multiple sources, DOM is a chemically complex pool, and only a small portion has been characterized (Benner 2002). The chemical composition of DOM will have a major impact on its biological availability and is strongly related to the source of the material. Labile DOM can be assimilated or respired rapidly (hours to days) by microbial communities, which are generally ignored in export estimates because they contribute a minor fraction of the sinking POM (e.g., Eppley and Peterson 1979). In contrast, semilabile DOM, or DOM that is resistant to rapid microbial degradation, can be exported from the euphotic zone through horizontal advection, vertical mixing, or sinking of aggregates (Peltzer and Hayward 1996; Passow 2000), which possibly results in the long-term removal of C and N from the euphotic zone.

Along with the lack of information concerning the sources and chemical composition of DOM, there is relatively little information concerning the spatial and temporal distribution of DOM and POM, particularly in upwelling systems. In a broad spatial survey conducted in Oregon coastal waters during the upwelling season, the highest concentrations of chlorophyll *a* (~10 μg L^{-1}) and POM (50–70 μmol L^{-1} particulate organic carbon [POC] and 7–8 μmol L^{-1} particulate organic nitrogen [PON]) were found in coastal waters influenced by upwelling (Hill 1999; Hill and Wheeler 2002). High dissolved organic carbon (DOC) concentrations (≥130 μmol L^{-1}) were found in both Columbia River plume water

and in shelf waters offshore of the upwelling front, whereas the highest dissolved organic nitrogen (DON) concentrations (7–10 μmol L^{-1}) were found in shelf waters offshore of the upwelling front. During a subsequent time-series study at a coastal Oregon site influenced by upwelling, Hill and Wheeler (2002) found that POM and DOM concentrations were highest during the upwelling season, which suggests that phytoplankton were a major source of the organic matter. Roughly 63% of the organic carbon produced in excess of deep water concentrations was in the form of DOC, which indicates a potentially pronounced role for DOM in terms of the fate of new production in the Oregon upwelling system.

In the present study, the production and partitioning of organic carbon and nitrogen were examined in deck incubations. Our goals were twofold. First, we wanted to document how organic matter is partitioned in upwelling-induced phytoplankton blooms. The development of blooms with different phytoplankton community compositions in the incubations facilitated an exploration of the effects of species composition on organic matter production and partitioning. We also wanted to begin to address the fate of nitrate-based production, because nitrate assimilation is frequently used as a proxy for new production in upwelling systems (Eppley and Peterson 1979). Whether newly produced organic matter accumulates primarily as DOM or POM will have profound implications for food-web structure and for understanding carbon and nitrogen cycles in the ocean.

Methods

Experiments were run on 6–25 August 2001. Water samples for two incubations (1 and 2; A and B in all figures) were collected from midshelf sites on a transect off northern Oregon (45.00°N, 124.02°W), where the shelf and region of active upwelling are relatively narrow. Water samples for the other two incubations (3 and 4; C and D in all figures) were collected from midshelf sites on transects off central Oregon (44.13°N, 124.28°W and 44.06°N, 124.33°W, respectively) in an area characterized by a broad shelf. Maps of the study region can be viewed at http://damp.oce.orst.edu/coast/summary.shtml.

For each incubation, triplicate 20-liter high-density polyethylene (HDPE) Cubitainers were filled with 1 liter of surface water inoculum and 19 liters of water from below the mixed layer (~28–70 m). Seawater was pumped directly into the Cubitainers from depth using a towed sled with a pump attached. Prior to being filled, Cubitainers were vigorously rinsed with 10% HCl followed by multiple rinses with deionized water (DIW). All incubations began in the early evening (0100–0400 GMT). Cubitainers were held in a deck incubator at in situ surface water temperatures of 11–15.5°C, with an average of 13.5°C. There were ~14 h of light and 10 h of darkness daily during the cruise, and daily integrated photosynthetically active radiation values at the surface ranged 15.0–52.0 mol quanta m^{-2} d^{-1} (mean, 31.6 ± 12.0 mol quanta m^{-2} d^{-1}). The incubator was covered with one layer of neutral density mesh screen that reduced light intensities to ~50% of surface intensities. Moderate mixing of samples occurred because of the motion of the boat, and the samples were vigorously mixed manually once or twice daily. Cubitainers were sampled daily in the early morning (1400–1700 GMT). Incubations lasted 7–8 d.

Biological analyses—Three different size fractions of chlorophyll were collected: whole water and <20 and <3 μm. Whole-water samples were vacuum filtered (<200 mm Hg) onto GF/F filters. Samples for <20 μm chlorophyll were gravity filtered through a 20-μm mesh screen and then vacuum filtered onto GF/F filters. Samples for <3 μm chlorophyll were first gravity filtered through a 20-μm mesh screen, vacuum filtered through a 3-μm polycarbonate filter (<200 mm Hg), then vacuum filtered onto a GF/F filter. After filtration, all samples were stored in glass Vacutainers and immediately frozen at −30°C until laboratory analysis. Chl *a* was extracted from the filters for ≥12 h in the dark at −20°C using 95% methanol. Fluorescence was measured with a Turner 10-au fluorometer. For the 3–20 μm size fraction, standard deviations were calculated by propagation of error using standard deviations from <20 and <3 μm chlorophyll size fractions (Bevington 1969). For the >20 μm size fraction, standard deviations were calculated by propagation of error using standard deviations from <20 μm and whole-water chlorophyll size fractions.

Chemical analyses—Nutrient samples were collected in acid-washed 30-ml HDPE bottles and immediately frozen at −30°C. Samples were processed within 4 months of collection. Samples were analyzed on a Technicon AA-II according to the standard wet chemical methods of Gordon et al. (1995). Standard curves with four different concentrations were run daily at the beginning and end of each run. Fresh standards were made prior to each run by diluting a primary standard with low-nutrient surface seawater. DIW was used as a blank, and triplicate DIW blanks were run at the beginning and end of each run, to correct for any baseline shifts. Nitrate was determined by subtracting nitrite values from nitrate plus nitrite (N+N) values. The standard deviation for nitrate was calculated by propagation of error using standard deviations for N+N and nitrite. Analytical errors, represented as the deviation of each point of the standard curve from a linear regression line, were 0.02 ± 0.03 μmol L^{-1} for phosphate, 0.05 ± 0.03 μmol L^{-1} for ammonium, 1.28 ± 0.78 μmol L^{-1} for silicate, 0.26 ± 0.17 μmol L^{-1} for N+N, and 0.02 ± 0.01 μmol L^{-1} for nitrite. Nutrient usage ratios are the slopes of nitrate versus phosphate or nitrate versus silicate prior to the first day of nitrate depletion and were determined from simple linear-regression models using the least-squares method for estimating the slope. Significance levels of the slopes were determined using two-sided *t*-tests.

Total nitrogen (TN) samples were collected in acid-washed 60-ml HDPE bottles and immediately frozen at −30°C until laboratory analysis. Samples were processed within 5 months of collection and were analyzed over 3 d. Organic nitrogen was converted to nitrate using a persulfate wet oxidation method (Libby and Wheeler 1997), which was then analyzed using a Technicon AA-II. Instrument calibration was performed daily using a standard curve prepared from triplicate-digested leucine standards at three concentrations. Fresh standards were made prior to each run by di-

luting a primary standard with artificial seawater. Digested artificial seawater was used as a blank, and the standard curve was corrected for the nitrogen content of the blank by determining the concentration of nitrogen in the persulfate solution and then calculating the amount of nitrogen in the artificial seawater. The artificial seawater nitrogen content was estimated as the difference between blank signal and persulfate signal. The average coefficient of variation for all TN replicates was 2.61% (±0.33%), and the highest observed coefficient of variation was 8.02%.

Total organic carbon (TOC) samples were collected in borosilicate vials with Teflon cap liners. Each vial contained ~5 ml of seawater that was preserved with 50 μl of 90% phosphoric acid. Samples were stored at room temperature until being processed 3 months later. Samples were analyzed over a 3-d period using the high-temperature catalytic combustion method on a Shimadzu TOC-5000A analyzer. Standard curves were run twice daily using a DIW blank and four concentrations of an acid–potassium phthalate solution. Five subsamples were taken from each water sample and injected in sequence. Variance between subsamples was ≤5.26% (mean, 2.62% [±1.19%]). Deep-water standards of known TOC concentrations were injected after every three to four samples (15–20 subsamples), to check for baseline shifts. For the 3 d of sample analysis, average daily TOC concentrations in the deep-water standard were 38.9, 40.1, and 41.7 μmol L^{-1}. Baseline drift was calculated from changes in the deep-water concentrations during a run, and a drift correction was applied to the raw data. The data were then normalized to a long-term average TOC concentration of the deep-water standard (~40.1 μmol L^{-1}). As an additional check to make sure that the system was working properly, Sargasso Sea deep-water standard (obtained from Dr. W. Chen, Certified Reference Materials Program, University of Miami) was injected once or twice during each run. The average TOC concentration in the Sargasso Sea deep water for the three runs was 45.2 ± 1.1 μmol L^{-1}, which indicates little systematic variation from day to day. When the coefficient of variation of the triplicates was >15%, a sample value was removed if it was >1 standard deviation away from the mean of the triplicates. Only one value was excluded out of 90 total measurements. The average coefficient of variation for all TOC replicates was 4.84% (±0.64%), and no replicates had a coefficient of variation >12.7%.

POC and PON were determined from material collected on precombusted GF/F filters. Water samples were prefiltered through a 202-μm mesh screen, to remove large zooplankton. Then, 500 or 1,000 ml of the filtered water was vacuum filtered (<200 mm Hg) onto precombusted GF/F filters. After filtration, samples were stored in glass Vacutainers and immediately frozen at −30°C until laboratory analysis. Samples were processed within 2 months of collection. Filters were fumed with concentrated hydrochloric acid, to remove inorganic carbon, and dried, followed by analysis using a 440HA CHN elemental analyzer (Control Equipment) calibrated with acetanilide. During analysis, filter blanks were run after every 9–10 samples. Filter blank averages were 18.4 ± 3.26 μg C and 0.33 ± 1.08 μg N, and these values were subtracted from each measured value as a filter blank correction. Carbon filter blanks averaged 24% of initial (day 0) POC samples and 2% of maximum POC samples for the four incubations. Nitrogen filter blanks were ≤6% of all PON samples. When the coefficient of variation of the triplicates was >15%, a sample value was removed if it was >1 standard deviation away from the mean of the triplicates. In all, six POC and three PON values were removed out of a total of 89 measurements. The average coefficients of variation for all POC and PON replicates were 6.48% (±0.68%) and 5.49% (±0.64%) respectively, and the highest observed coefficients of variation for POC and PON replicates were 13.3% and 12.5%, respectively.

DON was determined by subtracting PON and dissolved inorganic nitrogen (DIN = $NH_4 + NO_3^- + NO_2^-$) values from TN values, as shown in Eq. (1).

$$\mathrm{DON} = \mathrm{TN} - \mathrm{PON} - \mathrm{DIN} \quad (1)$$

The standard deviation for DON was calculated by propagation of error using standard deviations for TN, PON, and DIN. The average coefficient of variation for all DON replicates was 17.1% (±2.14%).

DOC was determined by subtracting POC values from TOC values, as shown in Eq. (2).

$$\mathrm{DOC} = \mathrm{TOC} - \mathrm{POC} \quad (2)$$

The standard deviation for DOC was calculated by propagation of error using standard deviations for TOC and POC. The average coefficient of variation for all DOC replicates was 13.8% (±1.96%). Most of the variation came from samples in which TOC concentrations were >100 μmol L^{-1}.

Results

Phytoplankton biomass, size structure, and nutrient usage—Phytoplankton blooms developed in all four incubations, and Chl *a* peaked in 4–6 d, depending on initial chlorophyll concentrations (Fig. 1). Maximum Chl *a* concentrations ranged 23–41 μg Chl *a* L^{-1}. The first three blooms were composed of large (>20 μm) cells (Fig. 1A–C), namely the diatom *Chaetoceros* sp. The last bloom was composed primarily of the small (~12 × 3 μm) diatom *Leptocylindrus minimus* (~60% of peak Chl *a*) (Fig. 1D), although some larger diatoms were present (~30% of peak Chl *a*). Initial nitrate values ranged 25–34 μmol L^{-1}. The ratio of nitrate to phosphate used ranged 13.1–15.6 (mean, 14.6 ± 0.55) (Table 1). Nitrate was drawn down below detection limits (~0.26 μmol L^{-1}) in each incubation, but phosphate was never depleted. The ratio of nitrate to silicate used ranged 0.84–1.69 (mean, 1.24 ± 0.25) in the microplankton blooms. However, the *L. minimus* bloom used ~2.55 μmol nitrate μmol $silicate^{-1}$ (Table 1). Chl *a* in the >20 μm size fraction began to decline immediately after nitrate depletion in all four incubations. However, chlorophyll in the <3 μm size fraction remained elevated or increased in two of the incubations after nitrate depletion (Fig. 1A,C). Furthermore, flow cytometric analysis confirmed that *Synechococcus* sp. and small eukaryotic phytoplankton abundances peaked 1–2 d after nitrate depletion (data not shown).

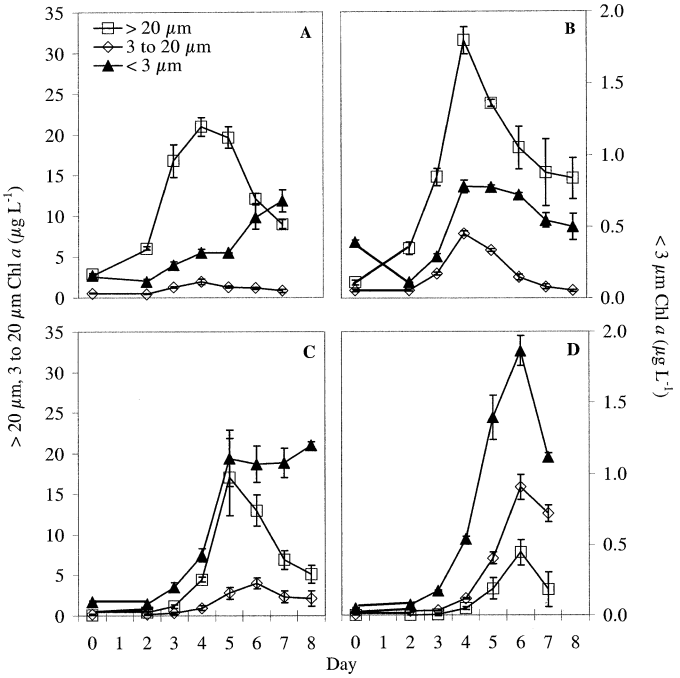

Fig. 1. Size-fractionated Chl *a* concentrations in deck incubations. (A and B) Incubations 1 and 2, from sites off northern Oregon. (C and D) Incubations 3 and 4, from sites off central Oregon. Error bars represent standard deviations.

Organic carbon and nitrogen—In all incubations, organic matter was initially partitioned mainly into the POM pool (~78%–100% of total organic matter [TOM]), which was nitrogen rich (C : N ~ 4–8) (Table 2). The accumulation of POM was concomitant with the development of phytoplankton blooms in each of the incubations (Figs. 2, 3). Significantly more POC accumulated in the microplankton blooms (Fig. 2A–C) (mean, 300 ± 12.1 μmol L^{-1}) than in the nanoplankton bloom (Fig. 2D) (mean, 240 ± 11.4 μmol L^{-1}; *t*-test, $P < 0.05$). Similarly, significantly more PON accumulated in the microplankton blooms (Fig. 3A–C) (mean, 25.4 ± 0.43 μmol L^{-1}) than in the nanoplankton bloom (Fig. 3D) (mean, 20.1 ± 0.63 μmol L^{-1}; *t*-test, $P < 0.05$). After nitrate depletion, the accumulated POM became enriched in carbon relative to nitrogen (Table 2) (C : N ~ 9–13.5). In three incubations, POC continued to increase by 44.0–131 μmol L^{-1} (mean, 83.7 ± 14.8 μmol L^{-1}) for ≥1 d (Fig. 2A,C,D). Significant increases in PON were observed in only two of the incubations after nitrate depletion (Fig. 3A,C). Those increases amounted to 5.75 ± 1.56 and 4.17 ± 3.11 μmol L^{-1}. In the other incubations, PON remained at a constant level (Fig. 3D) or decreased (Fig. 3B).

No DOM accumulated in nitrate-replete conditions except in the second incubation, when a relatively small (~14.0–26.4 μmol L^{-1} DOC and 2.70–6.30 μmol L^{-1} DON), but statistically significant (*t*-test, $P < 0.05$) amount of nitrogen-rich (C : N ~4–5) DOM accumulated. After nitrate depletion, carbon-rich DOM (C : N ≥ 16) rapidly accumulated over a 1-d period that coincided with nitrate depletion (Figs. 2, 3; Table 2). Although the timing of the DOM increase was similar between incubations, the magnitude of the DOM accumulation was significantly less (*t*-test, $P < 0.05$) in the nanoplankton bloom (Figs. 2D, 3D) (41 μmol L^{-1} DOC and 2.8 μmol L^{-1} DON) than in the microplankton blooms (Figs. 2A–C, 3A–C) (109–161 μmol L^{-1} DOC and 6.3–9.4 μmol L^{-1} DON). Accumulated DOC made up 18%–50% of TOC produced in the microplankton blooms but only 15% in the nanoplankton bloom. Approximately 42% of the initial accumulation of DOC and 80% of the initial accumulation of DON was drawn down the following day in the first incubation but subsequently increased to near maximal values (Figs. 2A, 3A). In the other three incubations, DOC concentrations remained constant (Fig. 2C) or increased (Fig. 2B,D) after the initial accumulation. In two of the microplankton blooms, the initial DON buildup was transient—up to 92% was removed by the following day (Fig. 3A,C). During the transient peak, DON accounted for 15%–30% of the accumulated TON pool in the microplankton blooms but only 7% in the nanoplankton bloom. Near the end of two of the incubations, DON subsequently increased by 3.60–8.67 μmol L^{-1} (mean, 6.14 ± 1.79 μmol L^{-1}) (Fig. 3A,B).

Calculated dissolved inorganic carbon assimilation—On the basis of measured concentrations of accumulated TOC and under the assumption of Redfield stoichiometry of 6.63 mol C mol nitrate^{-1}, ~70%–157% more carbon was fixed than can be supported by nitrate (Table 3). Most of the excess carbon fixation occurred immediately after the depletion of nitrate. However, ~20%–69% of the excess carbon fixation occurred ≥1 d after nitrate was initially depleted. In three of the incubations (1, 3, and 4), the excess carbon that was fixed in the days after nitrate depletion was measured mostly as POM. The increase in the C : N content of the POM after nitrate depletion ranged 9.90–25.8 in those incubations. In the other incubation (2), the excess carbon that was fixed after nitrate depletion was measured as DOM.

Discussion

As was expected, diatom blooms developed in all four incubations, consistent with patterns of phytoplankton bloom formation in coastal upwelling systems (Chavez and Smith 1995). All of the diatom blooms appear to have been terminated by nitrate depletion, regardless of species composition. The ratio of nitrate to phosphate assimilation was similar in all blooms (13.1–15.6). However, the *L. minimus* bloom used about one half as much silicate per unit of nitrate, as did the *Chaetoceros* sp. blooms, which perhaps reflects morphological or physiological differences between the species. After nitrate depletion, chlorophyll in the <3 μm size fraction remained elevated or increased in two of the four incubations (Fig. 1A,C). Abundances of *Synechococcus* sp. and small eukaryotic phytoplankton, determined by flow cytometric analysis, also peaked 1–2 d after nitrate depletion, which indicates that the cells might have been using regenerated nitrogen or DON (data not shown). There is precedent for phytoplankton growth using both ammonium and organic compounds in upwelling systems, particularly, although not exclusively, among cyanobacteria and nanoflagellates (Kokkinakis and Wheeler 1988; Probyn et al. 1990; Antia et al. 1991).

Table 1. Nutrient concentrations (μmol L^{-1}) and nutrient usage ratios in deck incubations. Values designated ''ND'' indicate that the sample was below limits of detection based on analytical error estimates (see ''Methods'' section). Ratios of nutrients used are the slopes of linear regressions of nitrate vs. phosphorous and nitrate vs. silicate prior to the first day of nitrate depletion, including data from all three replicate carboys. In some cases, only duplicate nitrate values were available.

Incubation number, day	NO_3^- ± SD	NO_2^- ± SD	NH_4^+ ± SD	$Si(OH)_4$ ± SD	PO_4^{3-} ± SD	N : P used ± SE (95% confidence interval)	N : Si used ± SE (95% confidence interval)
1							
0	30.79 ± 2.05	0.29 ± 0.02	1.08 ± 0.35	43.68 ± 3.77	2.64 ± 0.14	14.62 ± 0.32	1.21 ± 0.09
2	28.35 ± 0.37	0.35 ± 0.00	ND	41.28 ± 0.11	2.41 ± 0.02	(13.86–15.38)	(0.99–1.42)
3	15.41 ± 1.44	0.40 ± 0.01	0.15 ± 0.09	31.61 ± 1.41	1.57 ± 0.10	$n = 9$	$n = 9$
4	ND	0.12 ± 0.00	0.34 ± 0.07	3.40 ± 1.79	0.46 ± 0.01	$p < 0.01$	$p < 0.01$
5	ND	0.13 ± 0.00	0.25 ± 0.00	3.96 ± 6.12	0.70 ± 0.08		
6	ND	0.07 ± 0.00	0.69 ± 0.71	ND	0.71 ± 0.06		
7	ND	0.06 ± 0.01	0.28 ± 0.04	ND	0.70 ± 0.01		
2							
0	30.99 ± 0.27	0.38 ± 0.00	2.85 ± 0.02	48.65 ± 0.27	3.01 ± 0.01	13.07 ± 0.36	0.84 ± 0.02
2	28.92 ± 0.28	0.40 ± 0.00	1.16 ± 0.20	43.85 ± 0.70	2.77 ± 0.03	(12.25–13.90)	(0.78–0.89)
3	21.71 ± 0.40	0.42 ± 0.00	0.09 ± 0.05	35.25 ± 0.15	2.11 ± 0.05	$n = 10$	$n = 10$
4	0.26 ± 0.07	0.14 ± 0.00	0.40 ± 0.03	10.58 ± 1.22	0.65 ± 0.02	$p < 0.01$	$p < 0.01$
5	ND	0.15 ± 0.01	0.39 ± 0.03	ND	0.76 ± 0.06		
6	ND	0.07 ± 0.00	0.31 ± 0.03	ND	0.69 ± 0.10		
7	ND	0.06 ± 0.00	0.29 ± 0.04	ND	0.67 ± 0.02		
8	ND	0.05 ± 0.01	0.40 ± 0.28	1.35 ± 0.88	0.72 ± 0.15		
3							
0	34.27 ± 0.47	0.16 ± 0.03	ND	49.36 ± 0.31	2.80 ± 0.03	15.04 ± 0.39	1.69 ± 0.13
2	33.35 ± 0.60	0.17 ± 0.02	0.16 ± 0.28	47.58 ± 2.54	2.75 ± 0.02	(14.19–15.89)	(1.41–1.98)
3	32.42 ± 0.54	0.21 ± 0.01	0.07 ± 0.04	49.54 ± 0.58	2.57 ± 0.04	$n = 15$	$n = 15$
4	28.46 ± 0.47	0.17 ± 0.02	0.06 ± 0.05	47.18 ± 0.55	2.27 ± 0.06	$p < 0.01$	$p < 0.01$
5	6.79 ± 3.41	0.21 ± 0.06	0.16 ± 0.02	34.54 ± 4.27	0.95 ± 0.21		
6	ND	0.06 ± 0.00	0.58 ± 0.30	17.05 ± 4.73	0.69 ± 0.06		
7	ND	0.05 ± 0.00	0.65 ± 0.28	10.95 ± 2.96	1.06 ± 0.14		
8	ND	0.05 ± 0.00	0.28 ± 0.19	9.25 ± 2.70	0.89 ± 0.06		
4							
0	24.98 ± 0.32	0.15 ± 0.00	0.06 ± 0.04	29.31 ± 0.27	1.99 ± 0.02	15.63 ± 0.23	2.55 ± 0.28
2	24.56 ± 0.38	0.16 ± 0.00	ND	28.71 ± 0.97	1.93 ± 0.05	(15.12–16.14)	(1.93–3.17)
3	23.72 ± 0.50	0.18 ± 0.00	ND	28.74 ± 0.70	1.92 ± 0.02	$n = 12$	$n = 12$
4	21.65 ± 0.13	0.12 ± 0.00	ND	28.09 ± 0.56	1.74 ± 0.04	$p < 0.01$	$p < 0.01$
5	12.05 ± 1.04	0.15 ± 0.02	ND	24.86 ± 1.48	1.17 ± 0.04		
6	ND	0.06 ± 0.00	0.20 ± 0.00	13.33 ± 0.16	0.38 ± 0.02		
7	ND	0.06 ± 0.00	0.21 ± 0.03	8.39 ± 0.43	0.51 ± 0.05		

Partitioning of organic matter—Our nitrogen budgets show that nitrogen was completely conserved in the first two incubations. There was no significant difference (*t*-test, $P < 0.05$) in TN concentrations between the beginning and end of incubations 1 and 2. However, in incubations 3 and 4, ~83.7% (±1.6%) and 85.8% (±1.2%) of initial TN concentrations were found at the end of the experiments. Most of the nitrogen that was lost during the third incubation disappeared after the peak of the diatom bloom. Thus, incomplete recovery could have been due to undersampling of particulate matter that settled out and did not get completely mixed prior to sampling or to the exclusion of large diatom chains from POM analysis because of prefiltration through a 202-μm mesh screen. Nearly all of the nitrogen that was lost (~4.5 μmol L^{-1}) during the fourth incubation disappeared between days 3 and 4, or prior to the peak of the phytoplankton bloom. Between those 2 d, DON also decreased by ~4 μmol L^{-1}. Although one could argue that the DON was being rapidly regenerated to ammonium, ammonium concentrations were near or below detection limits for the first 5 d of that incubation. Additionally, between days 3 and 4, when the DON decrease occurred, bacterial abundances only increased slightly (from 0.97×10^6 to 1.15×10^6 cells ml^{-1}). Using those abundances and an average nitrogen content for coastal bacteria of 5.7 fg $cell^{-1}$ (Fukuda et al. 1998), bacterial particulate nitrogen would have increased from 0.40 ± 0.02 to 0.47 ± 0.03 μmol L^{-1}. Thus, it is unlikely that bacterial incorporation could account for the DON decrease. Unless phytoplankton uptake caused the DON draw-down, it seems likely that the disappearance of

Table 2. Partitioning of accumulated organic matter (as % of total accumulated organic matter) and elemental composition of the organic matter. Values designated ''NS'' indicate no significant accumulation. Values designated ''*'' indicate accumulation of either DOC or DON but not both. Dashed lines indicate when nitrate went to depletion.

Incubation number, day	% POC	% DOC	% PON	% DON	$C:N_{POM} \pm SD$	$C:N_{DOM} \pm SD$
1						
0						
1						
2	100	0	100	0	4.33 ± 0.40	NS
3	100	0	100	0	5.25 ± 0.11	NS
4	60	40	74	26	8.39 ± 0.54	16.3 ± 8.65
5	82	18	100	0	11.8 ± 0.57	*
6	69	31	81	19	11.4 ± 0.30	22.5 ± 16.6
7	74	26	80	20	11.4 ± 0.51	16.7 ± 10.0
2						
0						
1						
2	88	12	100	0	6.87 ± 0.98	*
3	79	21	78	21	5.21 ± 0.12	5.17 ± 5.19
4	88	12	81	20	7.27 ± 0.25	4.18 ± 4.20
5	71	29	85	15	12.8 ± 0.89	28.9 ± 15.3
6	64	36	77	23	13.3 ± 0.83	24.7 ± 6.18
7	60	40	74	26	13.5 ± 1.42	26.0 ± 6.94
8	50	50	60	40	12.5 ± 0.34	18.4 ± 4.66
3						
0						
1						
2	100	0	100	0	7.97 ± 1.70	NS
3	100	0	100	0	6.12 ± 0.76	NS
4	100	0	100	0	4.96 ± 0.53	NS
5	100	0	100	0	5.13 ± 0.04	NS
6	55	46	70	30	8.99 ± 1.15	17.2 ± 7.86
7	65	35	100	0	9.28 ± 0.56	*
8	65	35	100	0	10.5 ± 0.90	*
4						
0						
1						
2	100	0	100	0	8.36 ± 7.46	NS
3	100	0	100	0	4.29 ± 0.58	NS
4	100	0	100	0	5.21 ± 0.25	NS
5	100	0	100	0	5.30 ± 0.18	NS
6	100	0	92	7	10.4 ± 0.76	*
7	85	15	100	0	11.9 ± 0.33	*

the DON and TN from the fourth incubation could have been due to the adsorption of the DON to the walls of the Cubitainers.

Initial POM and DOM concentrations were similar to the deep-water concentrations seen by Hill and Wheeler (2002) off the Oregon coast, except in the first incubation, where initial DOM concentrations were relatively high. The day after the first incubation began, a vertical profile from a more nearshore station showed elevated DOC (127–252 μmol L^{-1}) and DON (19–24 μmol L^{-1}) concentrations throughout the water column (P.A.W. unpubl. data). This high-DOM water could have been the source of the high initial DOM concentrations in the first incubation.

Newly produced, nitrogen-rich organic matter (C : N ~ 4–8) was partitioned mainly into the particulate pool (~78%–100% of TOM produced) as the phytoplankton blooms developed. Significant partitioning of organic matter into POM has been observed in high-latitude coastal waters (Wheeler et al. 1997; Carlson et al. 1998), although it has rarely been demonstrated in temperate coastal waters. Most studies in temperate systems have shown that bloom-derived organic matter accumulates mainly as DOM over the growing season (Williams 1995; Carlson et al. 1998), and it has been suggested that major partitioning of organic matter as DOM is a common phenomenon in marine waters (Sondergaard et al. 2000). However, during the peak of an episodic phyto-

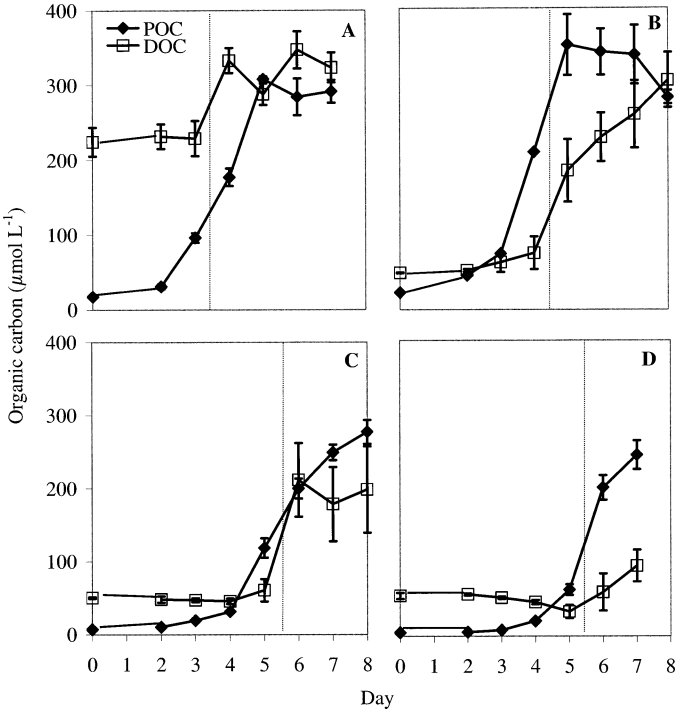

Fig. 2. Temporal distribution and partitioning of organic carbon in deck incubations. Dashed lines indicate when nitrate went to depletion. (A–D) Incubations 1–4, respectively. Error bars represent standard deviations.

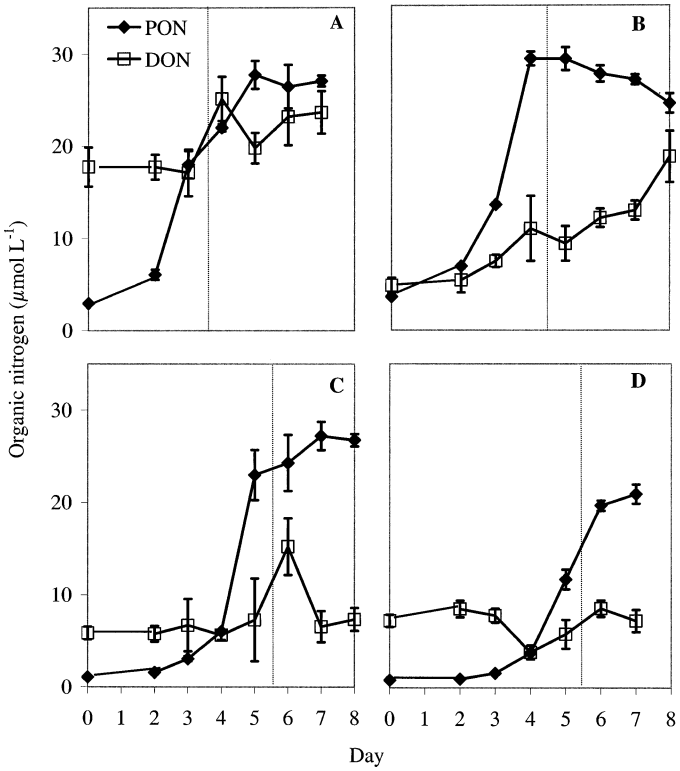

Fig. 3. Temporal distribution and partitioning of organic nitrogen in deck incubations. Dashed lines indicate when nitrate went to depletion. (A–D) Incubations 1–4, respectively. Error bars represent standard deviations.

plankton bloom off coastal Oregon, ~50%–75% of accumulated organic matter was in particulate form in the upper 10 m of the water column (Hill 1999). Furthermore, as the bloom developed, DOM concentrations remained steady or decreased (Hill 1999). In a study of an embayment affected by coastal upwelling, Doval et al. (1997) found that ~60% and 70% of accumulated organic matter was in the form of POC and PON, respectively. In our experiments, DOM only accumulated in one incubation prior to nitrate depletion. A small amount (~12%–21% of accumulated organic matter) of nitrogen-rich DOM (C : N ~ 4–5) accumulated in the second incubation, which was dominated by *Chaetoceros* sp. Although grazing or viral lysis could have contributed to the DOM, phytoplankton excretion may also have been a source. It has been suggested that the diffusive loss of small amounts of DOM may be a common characteristic of phytoplankton physiology, even among presumably healthy cells (Bjornsen 1988). However, the overall magnitude and ecological significance of such release is still subject to debate (Williams 1990), and our results suggest that DOM is a small fraction of primary production during the exponential growth of coastal phytoplankton blooms.

Immediately after nitrate depletion, large amounts of carbon-rich DOM (C : N $\geq$ 16) appeared in the three microplankton blooms, with DOC representing 38% ($\pm$8.5%) of accumulated TOC and DON representing 24% ($\pm$8%) of accumulated TON. Although there are numerous mechanisms by which DOM can be produced, our results suggest that the DOM accumulation was related to the onset of nutrient limitation of the phytoplankton blooms. The release of DOM by phytoplankton blooms that have become nutrient limited has been demonstrated in other marine systems (Lancelot 1983; Obernosterer and Herndl 1995). Phytoplankton cells often accumulate carbohydrates during exponential growth (Myklestad et al. 1989). At the transition between exponential and stationary growth phases or between nutrient-replete and -depleted conditions, phytoplankton are known to release large amounts of the accumulated dissolved carbohydrates, mainly as polysaccharides (Ittekkot et al. 1981; Myklestad et al. 1989; Biddanda and Benner 1997; Meon and Kirchman 2001). Empty diatom frustules were observed in fixed samples taken from several of our incubations after nitrate depletion, which indicates that cell lysis or grazing contributed in part to the accumulation of DOC. However, increases in TOC concentrations after nitrate depletion imply that photosynthetic carbon fixation continued for several days. Nitrogen limitation affects the enzyme functioning of phytoplankton photosynthetic carbon metabolism and ultimately leads to a decreased ability of cells to dissipate light energy (Turpin 1991). It has been proposed that the release of carbohydrates serves as an adaptive function in phytoplankton, in that it protects nutrient-limited cells growing in high light conditions from damage to their photosynthetic machinery by accommodating reductant supplied by light reactions (Wood and Van Valen 1990). Additionally, carbohydrate release has been implicated in aggregate formation (Passow et al. 1994), which in turn has been proposed as an adaptive mechanism by which diatom seed

Table 3. Potential amount of CO_2 fixed, under the assumption of 6.625 mol CO_2 fixed per mol NO_3^- assimilated, in comparison to net accumulated TOC (μmol L^{-1}). Dashed lines indicate when nitrate went to depletion.

Incubation number, day	NO_3^- (μmol L^{-1})	Potential CO_2 fixed (μmol L^{-1})	Average CO_2 ± SD	Accumulated TOC ± SD
1				
0	28.4	188	204 ± 13.6	
	31.8	211		
	32.2	213		
2				20.9 ± 35.1
3				83.4 ± 39.0
4				269 ± 25.2
5				354 ± 30.0
6				390 ± 20.8
7				373 ± 11.3
2				
0	30.7	203	205 ± 1.79	
	31.1	206		
	31.1	206		
2				25.8 ± 0.95
3				65.8 ± 13.2
4				213 ± 22.1
5				464 ± 8.67
6				499 ± 9.63
7				526 ± 21.2
8				527 ± 34.9
3				
0	33.7	223	227 ± 3.11	
	34.5	229		
	34.6	229		
2				2.10 ± 5.13
3				8.70 ± 1.69
4				18.9 ± 3.20
5				125 ± 6.74
6				351 ± 47.7
7				370 ± 48.4
8				418 ± 9.51
4				
0	24.8	164	165 ± 2.11	
	25.2	167		
2				3.36 ± 5.36
3				0.75 ± 5.79
4				6.94 ± 2.17
5				36.6 ± 7.07
6				201 ± 19.9
7				281 ± 8.98

stocks are maintained in coastal upwelling regions (Smetacek 1985).

Although the DOM released by the microplankton blooms was carbon rich, there was a considerable increase in DON. The release of DON by nitrogen-limited phytoplankton seems somewhat paradoxical, in that the cells are releasing a limiting resource and are also supplying substrate for bacterial competitors. However, DON release, accounting for 25%–41% of nitrogen taken up by phytoplankton, has been demonstrated in several different types of marine systems (Bronk et al. 1994). Obviously, DON release due to cell lysis would be unavoidable, as would DON release due to grazing. Several studies have demonstrated DON accumulation during and after phytoplankton blooms and have attributed a large portion of the accumulation to grazing (Bronk et al. 1998; Bronk and Ward 1999). However, numerous other studies have demonstrated the release of varying quantities of amino acids by phytoplankton at the transition from the exponential to the stationary growth phase and in the absence of grazing (Poulet and Martin-Jezequel 1983; Admiraal et al. 1986; Martin-Jezequel et al. 1988; Myklestad et al. 1989). In particular, Admiraal et al. (1986) observed a transient release of amino acids by the diatom *Thalassiosira excentrica* during the transition from exponential to stationary growth, suggesting that the release was due to a reduction in cell growth and metabolism.

In contrast to the incubations dominated by microplankton, relatively little DOC or DON accumulated in the nanoplankton bloom after nitrate depletion. One possible explanation for less DOM accumulation during the nanoplankton bloom is that there might have been a much tighter coupling between the DOM released and bacterial consumers than in the microplankton blooms. However, this scenario is not necessarily reflected in terms of bacterial abundance, which was relatively low compared with two of the other incubations (data not shown). A more plausible explanation would be that there are differences in the size of intracellular DOM pools between the phytoplankton species (Martin-Jezequel et al. 1988), thus leading to differential release of DOM after nitrate limitation (Hellebust 1965). In terms of intracellular composition, Myklestad (1974) and Martin-Jezequel et al. (1988) observed differences of several orders of magnitude in cellular carbohydrate and amino acid concentrations among different species of diatoms. These differences could explain, to some degree, differences in the percentage and magnitude of photoassimilated carbon and assimilated nitrogen excreted by different species of diatoms (Hellebust 1965; Admiraal et al. 1986).

Biogeochemical implications—The partitioning of primary production into either POM or DOM will have major consequences for the fate of that primary production by affecting export pathways. The results of our study and studies in other coastal systems suggest that POM can be a significant fraction of total primary production. The removal of POM from the euphotic zone can occur through sinking of the POM, vertical mixing of particles out of the euphotic zone, or horizontal transport due to advection. Elevated POM concentrations in bottom waters of the Oregon continental shelf suggests that there is a significant sinking flux of organic matter (Karp-Boss et al. unpubl. data). In addition to the large accumulation of POM, we also saw significant accumulation of DOM after nitrate depletion of the phytoplankton. Phytoplankton bloom decay in Oregon coastal waters is frequently attributed to the depletion of nitrate after the cessation of upwelling (Wroblewski 1977; Corwith and Wheeler 2002). Excluding sampling conducted during a transient bloom, Hill and Wheeler (2002) found that ~63%

of net excess production of organic carbon accumulated as DOC during the upwelling season in coastal Oregon waters, suggesting that some DOM is released by primary producers, although it is unclear how much is released before cells sink out of the euphotic zone. The accumulation of large amounts of phytoplankton-derived DOC (Williams 1995) and DON (Bronk et al. 1994) has been demonstrated in field studies conducted in other marine systems. Although it appears that the DON accumulation was transient in two of the four incubations in our study, little net change in accumulated DOC was observed. In a review of four different marine systems, Williams (1995) observed a significant long-term (months) accumulation of carbon-rich DOM and attributed it to the inability of bacteria to remineralize the DOM because of nitrogen limitation. However, the long-term accumulation of DOC in surface waters off Oregon during the upwelling season is unlikely, given the dynamics of the alongshore and upwelling circulation (Smith 1995). Investigations are currently under way to examine alongshore and cross-shelf variations in POM and DOM off Oregon, to better understand which physical processes influence the fate of organic material during the upwelling season.

Excess carbon fixation—Significantly more carbon was fixed than would be predicted on the basis of Redfield stoichiometries of carbon consumption to nitrate assimilation by phytoplankton. Approximately 70%–157% more carbon was fixed than would be predicted, with >20%–69% of the excess carbon fixation occurring after nitrate depletion. Photosynthetic carbon fixation above that predicted on the basis of nitrate uptake has been demonstrated in situ (Sambrotto et al. 1993). In a laboratory study, Engel et al. (2002) demonstrated excess carbon fixation by an experimental diatom bloom on the order of 72% more than predicted by nitrate assimilation, with nearly 100% of the excess fixed carbon going into the POM pool. Part of the POM pool (~40%) was determined to be TEP, a mucous-like substance that forms abiotically from dissolved carbohydrates (Passow 2000). Thus, TEP is carbon rich ($C:N \geq 26$) (Engel and Passow 2001) and forms mainly after phytoplankton blooms become nutrient limited (Corzo et al. 2000; Engel et al. 2002). Because part of the TEP was measured as POM, rapid transformation of dissolved compounds into particulate material must have occurred. After nitrate depletion, large amounts of carbon-rich DOM ($C:N \geq 16$) accumulated in our incubations, and diatom aggregates loosely held together by a mucous-like substance were observed in the first three incubations, consistent with TEP production. Although some of the excess fixed carbon accumulated as DOC, it also accumulated as POC, which suggests either intracellular storage of the excess carbon or release as DOM and rapid transformation of the DOM into TEP-like particles. Aggregation of the cells or TEP-like material could be a mechanism by which excess fixed carbon is rapidly exported from the surface ocean. However, because little is known about the fate of sinking aggregates in situ, more work is needed to examine processes that might disrupt or breakdown aggregates prior to their sinking out of the euphotic zone (Smith et al. 1992).

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