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# Multiyear increases in dissolved organic matter inventories at Station ALOHA in the North Pacific Subtropical Gyre

*Matthew J. Church*[1] *and Hugh W. Ducklow*
School of Marine Science, College of William and Mary, Gloucester Point, Virginia 23062

*David M. Karl*
School of Ocean and Earth Science and Technology, Department of Oceanography, University of Hawaii, Honolulu, Hawaii 96822

*Abstract*

The inventories and dynamics of dissolved organic matter (DOM) in the surface water at Station ALOHA were analyzed from the Hawaii Ocean Time-series (HOT) data set for the period 1989–1999. Euphotic zone, depth-integrated (0–175 m) concentrations of dissolved organic carbon (DOC), nitrogen (DON), and phosphorus (DOP) were temporally variable. In particular, during the period 1993–1999, concentrations of DOC and DON increased while inventories of DOP remained unchanged. DOC inventories increased by 303 mmol C $m^{-2}$ $yr^{-1}$, a value equivalent to approximately 2% of measured primary production ($^{14}C$ method) at this site. DON increased at 11 mmol N $m^{-2}$ $yr^{-1}$, resulting in a mean molar DOC : DON ratio of 27.5 for the accumulated DOM. Accumulation of DOC and DON without corresponding accumulation of DOP resulted in changes to the bulk organic C : N : P stoichiometry; bulk DOC : DOP ratios increased 16% and DON : DOP ratios increased by 17%. These results indicate that a small fraction of the annually produced organic matter escaped biological utilization on time scales of months to years. More importantly, the accumulated DOM inventories grew progressively enriched in C and N relative to P. Fundamental changes in the North Pacific Subtropical Gyre (NPSG) habitat appear to have altered microbial processes that regulate organic matter fluxes. Considered together, the long-term increases in DOC and DON inventories are consistent with previous observations, indicating that a recent reorganization of plankton community dynamics may have altered organic matter cycling in this ecosystem.

Dissolved organic matter (DOM) in seawater constitutes one of the largest exchangeable pools of reduced carbon on Earth, so accurate quantification of DOM inventories and fluxes is essential for understanding oceanic carbon cycling (Carlson et al. 1994; Ducklow et al. 1995; Williams 1995). Efforts to quantify carbon fluxes in oligotrophic marine ecosystems indicate that significant fractions of organic carbon may cycle through DOM pools (Carlson et al. 1994; Emerson et al. 1997; Carlson et al. 1998). At Station ALOHA in the North Pacific Subtropical Gyre (NPSG), the dissolved carbon (C), nitrogen (N), and phosphorus (P) inventories in the photic zone represent 98, 95, and 94% of the total organic matter inventories, respectively.

Three primary classes of bulk DOM have been defined based on their temporal lability in the marine environment: (1) labile DOM with turnover times of hours to days, (2) semilabile DOM that turns over on seasonal to annual time scales, and (3) nonlabile DOM inventories that cycle on time scales of hundreds to thousands of years (Kirchman et al. 1993). The ultimate source of DOM in the open ocean is marine primary production so across finite time and space scales, DOM production should covary with primary production. However, the exact pathways of DOM production and utilization are still poorly constrained (Ducklow and Carlson 1992). DOM is an operationally defined term used here to describe measured pools of organic carbon, nitrogen,

[1] Corresponding author (mattc@vims.edu).

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and phosphorus that pass through a microfine glass fiber filter (nominal pore size of 0.7 $\mu$m).

Investigations in the oligotrophic NPSG indicate that recent changes in the autotrophic community structure may have significantly altered the cycling of organic matter in this ecosystem. In particular, the phytoplankton community, once dominated by eukaryotes, appears to have shifted to a phototrophic community dominated by smaller, prokaryotic cells such as *Prochlorococcus* and *Synechococcus.* Karl (1999) describes this reorganization of the phototrophic community from eukaryotes to prokaryotes as a domain shift. One result of this shift is an apparent doubling of both chlorophyll *a* (Chl *a*) inventories and rates of $^{14}C$ primary production (Venrick et al. 1987; Karl 1999; Karl et al. 2001*a*). In addition, rates of nitrogen fixation and abundance of nitrogen-fixing microorganisms are hypothesized to have increased in the past decade, potentially altering the elemental stoichiometry of dissolved and particulate matter inventories in the NPSG (Karl et al. 1995, 1997). Determining the effects of such an ecological reorganization on organic matter inventories is crucial to assessing how community structure and nutrient cycling define the magnitude of carbon export and sequestration in oceanic ecosystems.

This paper examines the variability of DOM in the surface ocean of the NPSG between 1989 and 1999. We focus our temporal analyses on the latter period of observations (1993–1999), where profound changes in DOM pool dynamics may reflect the reorganization of the NPSG food web. During this period, the bulk DOM pool underwent significant alteration of varying amplitude and periodicity. Such alterations appear consistent with previously hypothesized changes in microbial community dynamics.

Table 1. Mean integrated properties of the euphotic zone (0–175 m) at Station ALOHA (1989–1999).

| Year | Temperature (°C)* | $NO_3^- + NO_2^-$ (mmol N $m^{-2}$)† | SRP (mmol P $m^{-2}$)‡ | Chlorophyll *a* (mg Chl *a* $m^{-2}$) | Primary production (mmol C $m^{-2}$ $d^{-1}$) |
|---|---|---|---|---|---|
| 1989 ($n$ = 4)§ | 16.8–26.5 | — | 18.20 | 26.68 | 38.18 |
| | | | (7.25) | (5.44) | (19.16) |
| 1990 ($n$ = 8) | 17.6–25.9 | 20.95 | 19.47 | 22.14 | 29.95 |
| | | (28.58) | (3.13) | (7.10) | (6.89) |
| 1991 ($n$ = 9) | 18.5–27.0 | 27.88 | 18.76 | 21.76 | 44.00 |
| | | (12.18) | (6.86) | (1.55) | (9.84) |
| 1992 ($n$ = 9) | 17.2–27.0 | 31.88 | 16.66 | 20.12 | 44.72 |
| | | (10.53) | (4.93) | (2.55) | (8.56) |
| 1993 ($n$ = 6) | 16.3–26.6 | 21.71 | 17.13 | 20.13 | 37.46 |
| | | (13.05) | (7.58) | (4.85) | (13.80) |
| 1994 ($n$ = 8) | 18.3–26.6 | 39.43 | 11.34 | 22.37 | 36.10 |
| | | (18.69) | (4.08) | (3.61) | (8.49) |
| 1995 ($n$ = 9) | 17.1–27.0 | 43.22 | 18.18 | 18.36 | 43.65 |
| | | (34.22) | (6.40) | (2.46) | (14.27) |
| 1996 ($n$ = 10) | 17.3–27.7 | 27.86 | 13.86 | 17.19 | 39.47 |
| | | (9.34) | (4.94) | (3.63) | (9.83) |
| 1997 ($n$ = 9) | 16.0–27.1 | 31.78 | 12.04 | 19.87 | 36.32 |
| | | (19.11) | (6.50) | (2.47) | (9.63) |
| 1998 ($n$ = 12) | 17.3–26.0 | 36.44 | 12.50 | 22.44 | 42.24 |
| | | (16.32) | (3.48) | (2.59) | (12.55) |
| 1999 ($n$ = 10) | 17.4–26.0 | 41.70 | 15.74 | 23.30 | 44.91 |
| | | (29.29) | (4.46) | (3.66) | (9.33) |

* Range of water column temperatures (0–175 m).
† Top numbers are mean integrated stocks; numbers in parentheses are standard deviations of the means.
‡ SRP, soluble reactive phosphorus.
§ $n$, annual number of observations from which mean integrated stocks were calculated. Typically 8–10 depths were sampled between the surface and 175 m for each observation. —, no data available.

## Methods

*Station location and sample collections*—All data were collected at Station ALOHA (22°45′N, 158°00′W) approximately 100 km north of Oahu as part of the HOT program. The complete data sets are available through the HOT Web site (http://hahana.soest.hawaii.edu/hot/hot_jgofs.html). Water samples for dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) determinations were collected at approximately monthly intervals from October 1988 to December 1999, whereas samples for dissolved organic carbon (DOC) were collected between January 1993 and December 1999. Comparative analyses of DOM inventories therefore focus on HOT cruises 44–110 (1993–1999) because these cruises provided complementary measurements of C, N, and P pool dynamics.

Water samples were collected from discrete depths using a 24-bottle conductivity–temperature–depth (CTD) rosette sampler (Karl et al. 2001*b*) with intensive sampling in the upper 200 m corresponding to the depths of primary production measurements. For this investigation, spatial analyses focus on the upper 175 m of the water column. We define this region as the euphotic zone (EZ) because it roughly corresponds to the depth of ~0.05% surface irradiance (175 m) and below which there is, on average, no net autotrophic production (Letelier et al. 1996).

*Measurements*—Descriptions of the methods used in this study can be found in Karl et al. (2001*b*) and Hebel and Karl (2001) and are also described in the electronic version of the HOT Laboratory and Field Protocols manual (http://hahana.soest.hawaii.edu/hot/protocols/ protocols.html). Analyses of nitrogen and phosphorus included total dissolved (TDN, TDP), inorganic (nitrate + nitrite [N + N], soluble reactive phosphorus [SRP]), and particulate nitrogen and phosphorus (PN, PP) inventories. DON and DOP were calculated by difference (i.e., DON = TN − ([N + N] + PN) and DOP = TP − (SRP + PP). DOC was calculated as the difference between total organic carbon (TOC) and particulate carbon (PC). Ambient EZ inventories of N + N and SRP reported in Table 1 were derived by the chemiluminescent method of Garside (1982) and by the MAGIC method described by Karl and Tien (1992), respectively.

Seawater for TOC analyses was subsampled directly into clean, sterile 15-ml polypropylene tubes (Corning #430052). Samples were immediately frozen (−20°C) until analyzed in the laboratory. Upon return to the laboratory, TOC samples were thawed to room temperature, shaken, and acidified with $H_3PO_4$ (final pH 2.0–2.5). Samples were purged for ~10 min using high-purity oxygen to remove inorganic carbon. One hundred microliters of sample were injected into the instru-

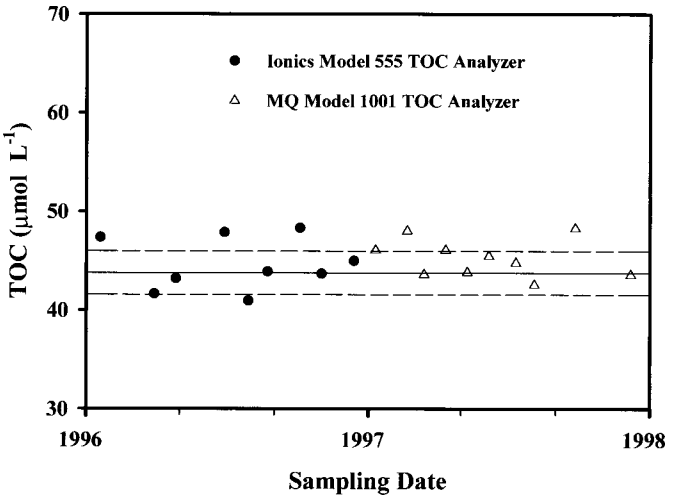



Fig. 1. Concentration of TOC at Station ALOHA from 3,000 m between 1996 and 1998. Closed circles are measurements of TOC using the Ionics Model 555 TOC analyzer; open triangles are measurements of TOC made using the MQ Model 1001 TOC analyzer. Solid line represents mean 3,000-m TOC concentration, whereas dotted lines are 1 standard deviation of the mean. No significant difference (ANOVA, $P > 0.05$) in the mean 3,000-m TOC concentration was observed, indicating comparable analytical baselines between the two instruments.

ment port. Between 1993 and 1996, TOC concentrations were measured using a commercially available Ionics Model 555 TOC analyzer modified with a LICOR Model 6252 infrared detector after removal of total inorganic carbon. Organic matter oxidation to $CO_2$ was facilitated by platinum catalysis. Instrument precision (based on the standard deviation of 3,000-m TOC measurements for the 1993–1996 period) was $\pm 4$ $\mu$M C. Beginning in January 1997, TOC concentrations were measured using a commercially available MQ Model 1001 TOC analyzer equipped with the same infrared detector. Similarly, analytical precision of the MQ instrument was $\pm 4$ $\mu$M C. Analysis of deep-sea (3000 m) TOC concentrations during the period of transition (1996–1997) between the Ionics instrument and the MQ system revealed no significant baseline offset between the two instruments (Fig. 1). Additional details of the operation of the Ionics and MQ instruments can be found in Tupas et al. (1994) and Qian and Mopper (1996), respectively.

Beginning in 1997, certified reference materials obtained from J. Sharp (University of Delaware) were analyzed and used for tracking instrument performance and assessing measurement accuracy. From 1993 to 1996, baseline blanks were determined by injection of UV-oxidized distilled water into the instrument; beginning in 1997, low-carbon water distributed from J. Sharp's laboratory served as the instrument blank. Blank values were subtracted from the measured seawater TOC values. Standards were prepared from either sucrose or phthalate stocks then analyzed with each sample run.

Complementary samples for PC, PN, and PP were collected during the same period (1989–1999), and the details of the sample collection and analyses can be found in Hebel and Karl (2001). Briefly, seawater was collected from the CTD rosette and subsampled into acid-cleaned polyethylene bottles. Samples were transferred through Tygon tubing containing a 202-$\mu$m screen mesh to exclude large particles. For PC and PN analyses, water was pressure filtered onto precombusted 25-mm glass fiber filters (Whatman GF/F). Variable volumes of seawater were filtered depending on the depth sampled (typically 4 liters in the upper 150 m and 10 liters from water >150 m). After filtration, filters were placed onto 2.5-cm$^2$ sections of combusted aluminum foil and stored at $-20$°C until analyzed in the laboratory by high-temperature combustion using commercially available instruments (Hebel and Karl 2001). Unlike PC and PN analyses, GF/F filters used for PP analyses were combusted and rinsed with HCl to reduce the P blank. Following filtration, PP samples were placed in acid-rinsed glass test tubes, 12 $\times$ 70 mm$^2$, covered with foil, and stored frozen. Upon return to the laboratory, PP filters were combusted, acid-hydrolyzed, and centrifuged and the supernatant was subsampled for SRP analyses as described below.

DON was estimated by subtraction of PN and N + N from TDN. Samples for DON were collected into 100-ml polyethylene bottles from the CTD sampling rosette and frozen until analysis. N + N samples were analyzed directly on a four-channel Technicon Autoanalyzer II (Armstrong et al. 1966). TDN samples were exposed to high-intensity (1200 W) UV radiation for 24 h at 84 $\pm$ 6°C and analyzed for N + N and $NH_4^+$ using the Technicon autoanalyzer. At the concentrations reported in this paper, the precision of the TDN measurement is $\pm 7\%$.

DOP was estimated by subtraction of SRP and PP from TDP. Samples of DOP were collected in polyethylene bottles and stored frozen. Prior to analyses, samples were thawed and divided into subsamples for independent measurements of SRP and TDP. SRP was measured using the standard molybdenum blue assay (Murphy and Riley 1962) modified for the Technicon autoanalyzer II system. TDP concentrations were determined using UV-photooxidation of seawater for 2 h followed by SRP autoanalysis of hydrolysis products using standard procedures (Armstrong et al. 1966). Calculating DOP by difference between TDP and SRP assumes a negligible dissolved inorganic polyphosphate pool. At the concentrations measured in this study, the precision of the TDP measurement is $\pm 14\%$.

Bacterial cell abundance was enumerated by flow cytometry using Hoechst 33342 as the fluorochrome (Monger and Landry, 1993). Briefly, samples were collected in 15-ml polypropylene centrifuge tubes, and then 1 ml was subsampled into Cryovials (Corning) containing 0.02 ml of 10% paraformaldehyde (final concentration 0.2%). The cryovials were quick-frozen in liquid nitrogen and stored at $-80$°C until analyzed. Prior to analysis, samples were thawed and cells were stained with Hoechst 33342 for ~2 hours and counted using a Coulter EPICS dual laser (225 mW UV and 1 W 488 nm) flow cytometer. Nonpigmented, presumably heterotrophic, Bacteria and Archaea were enumerated by stained DNA fluorescence and forward-angle light scattering (FALS), a proxy for cell size, using the software CYTOPC (Vaulot 1989).

Table 2. Interannual variation in integrated (0–175 m) organic matter stocks, stoichiometric ratios, and bacterial abundance at Station ALOHA (1989–1999).*†

| Year | DOC (mmol C $m^{-2}$) | DON (mmol N $m^{-2}$) | DOP (mmol P $m^{-2}$) | Bacteria ($10^{11}$ cells $m^{-2}$) | DOC : DON | DOC : DOP | DON : DOP |
|---|---|---|---|---|---|---|---|
| 1989 ($n$ = 9)‡ | — | 873.6 | 30.0 | — | — | — | 29.8 |
| | | (56.9) | (3.3) | | | | (4.3) |
| 1990 ($n$ = 8) | — | 739.6 | 26.8 | — | — | — | 27.8 |
| | | (103.5) | (2.4) | | | | (4.2) |
| 1991 ($n$ = 10) | — | 888.9 | 33.2 | 623.8 | — | — | 27.1 |
| | | (69.7) | (5.4) | (87.8) | | | (3.2) |
| 1992 ($n$ = 11) | — | 976.5 | 37.6 | 564.9 | — | — | 26.3 |
| | | (27.7) | (4.2) | (125.5) | | | (3.1) |
| 1993 ($n$ = 6) | 13636.2 | 924.6 | 33.7 | 659.4 | 14.8 | 408.6 | 27.6 |
| | (859.2) | (69.6) | (4.3) | (248.8) | (1.0) | (49.3) | (2.4) |
| 1994 ($n$ = 9) | 14358.18 | 913.4 | 37.3 | 662.9 | 15.8 | 400.0 | 25.1 |
| | (1302.0) | (48.1) | (5.9) | (125.7) | (1.7) | (112.8) | (4.8) |
| 1995 ($n$ = 9) | 14750.0 | 923.4 | 39.0 | 651.8 | 16.1 | 390.4 | 24.0 |
| | (1153.1) | (100.3) | (5.6) | (74.5) | (2.1) | (97.6) | (3.3) |
| 1996 ($n$ = 10) | 15054.8 | 948.8 | 34.5 | 855.6 | 15.9 | 439.4 | 27.7 |
| | (1446.0) | (43.4) | (2.7) | (161.7) | (1.8) | (55.7) | (2.5) |
| 1997 ($n$ = 10) | 15702.1 | 968.7 | 37.8 | 697.6 | 16.3 | 427.7 | 26.2 |
| | (942.5) | (82.3) | (6.7) | (134.9) | (1.8) | (80.4) | (3.7) |
| 1998 ($n$ = 12) | 15414.2 | 999.5 | 32.5 | 556.7 | 15.4 | 483.4 | 31.4 |
| | (1012.3) | (41.2) | (4.9) | (122.4) | (0.9) | (78.4) | (4.9) |
| 1999 ($n$= 10) | 15621.3 | 954.5 | 35.2 | 645.3 | 16.4 | 478.8 | 29.2 |
| | (567.5) | (54.2) | (9.3) | (120.1) | (1.2) | (154.3) | (9.8) |
| Significance§ | $P < 0.001$ | $P < 0.001$ | $P < 0.001$ | ns | ns | ns | $P < 0.05$ |
| Regression‖ | DOC = 0.83x + 12200 | DON = 0.03x + 840 | ns | ns | ns | DOC : DOP = 0.04x + 382 | ns |
| | $r^2 = 0.25$ | $r^2 = 0.10$ | | | | $r^2 = 0.09$ | |
| | $P < 0.0001$ | $P < 0.01$ | | | | $P < 0.05$ | |

* DOC, dissolved organic carbon; DON, dissolved organic nitrogen; DOP, dissolved organic phosphorus.

† Values presented are mean annual integrated (0–175 m) inventories of DOC, DON, and DOP. Numbers in parentheses are standard deviations of the mean integrated inventory. —, no data available.

‡ $n$, number of annual observations from which mean integrated stocks were calculated. Typically 8–10 depths were sampled between the surface and 175 m for each observation.

§ One-way ANOVA testing interannual differences in specified inventories and ratios. Statistical tests based on integrated inventories from each cruise grouped by year. Significance determined at $P < 0.05$. ns, $P > 0.05$.

‖ Model 1 linear regression where x is days since 1 January 1993. ns, regression not significant at $P < 0.05$.

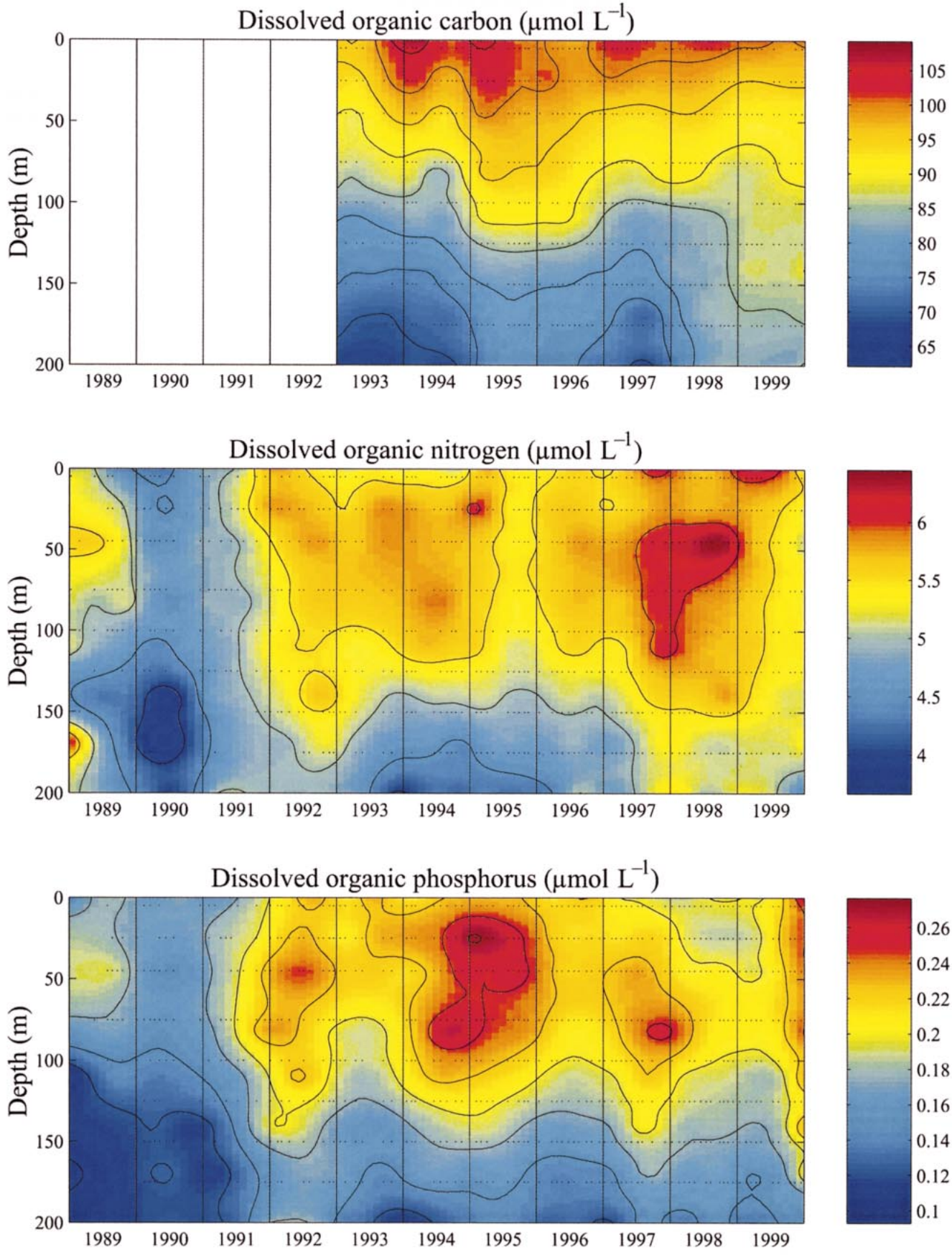
*Data analysis*—Areal standing inventories were calculated for the 0–175-m depth range using trapezoidal integration with linear interpolation between the discrete samples. Statistical testing was performed using Minitab 4.0. Statistical comparisons were based on one-way analysis of variance (ANOVA) and, for temporal trends, Model 1 linear regression analyses. The latter tests were performed on the depth-integrated DOM inventories versus time. All ANOVA statistical tests were based on integrated values from the monthly observations rather than on seasonally or annually averaged data. Significance was evaluated at the $P < 0.05$ level.

## Results

*Station ALOHA and the NPSG*—The prominent physical, chemical, and biological water column dynamics at Station ALOHA have been well characterized (*see* Karl 1999); selected data are summarized in Table 1. Surface-water temperatures are perennially warm (>20°C) but seasonally variable. Inorganic major nutrients ($NO_3^-$ and $HPO_4^{2-}$) are consistently low in the surface water (<0.1 $\mu$M), increasing at the top of the permanent nutricline (typically near the 150-m depth horizon) (Karl et al. 2001*b*). Phytoplankton abundance at Station ALOHA is dominated (>95% by cell num-

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Fig. 2. Concentration ($\mu$mol $L^{-1}$) versus depth (m) contour plots of (top) dissolved organic carbon (1993–1999), (center) dissolved organic nitrogen (1989–1999), and (bottom) dissolved organic phosphorus (1989–1999) in the upper EZ at Station ALOHA. The dark solid circles indicate depths and dates of sample collections.


Dissolved organic carbon (μmol L$^{-1}$)
Depth (m)
0
50
100
150
200
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
105
100
95
90
85
80
75
70
65
Dissolved organic nitrogen (μmol L$^{-1}$)
Depth (m)
0
50
100
150
200
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
6
5.5
5
4.5
4
Dissolved organic phosphorus (μmol L$^{-1}$)
Depth (m)
0
50
100
150
200
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1

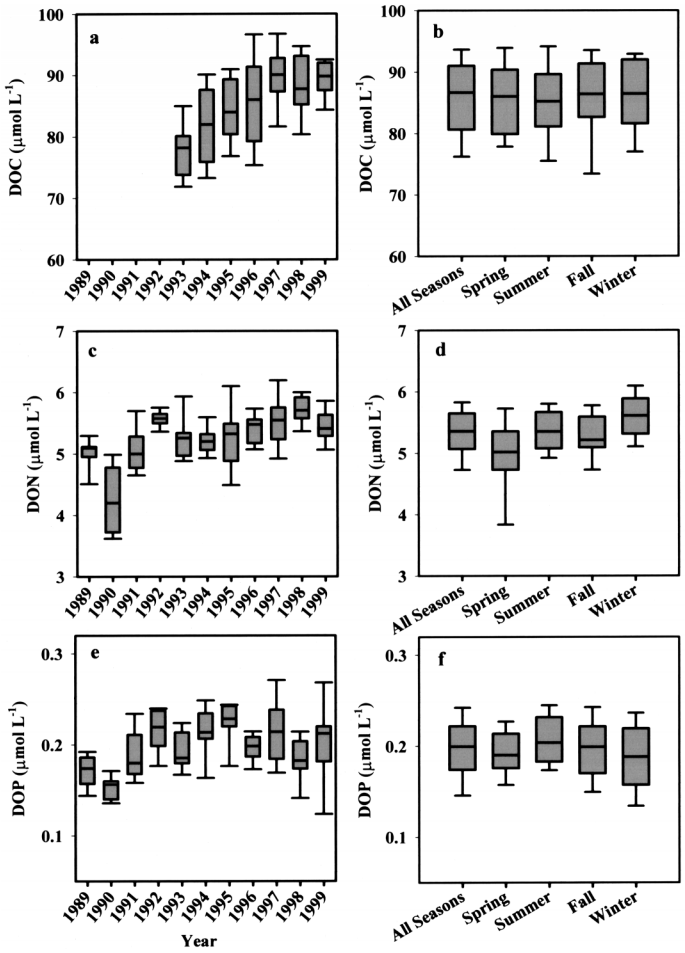



Fig. 3. Mean interannual changes in euphotic zone DOM concentrations (left panels) and seasonal climatology (right panels) based on full data sets. Boxes represent annual and seasonal (quarterly) divisions of DOM stocks. The line inside the box indicates the annual or seasonal mean, and the upper and lower boundaries of each box are the 75th and 25th percentiles, respectively. The capped bars show the 10th and 90th percentiles of the data. **All Seasons** is the total mean stock for the entire data set (DOC 1993–1998, DON and DOP 1989–1999) without seasonal divisions; seasonal classifications were defined as: **Spring**—March, April, May; **Summer**—June, July, August; **Fall**—September, October, November; and **Winter**—December, January, February. Mean EZ concentrations calculated as integral inventories divided by the 175-m depth interval.

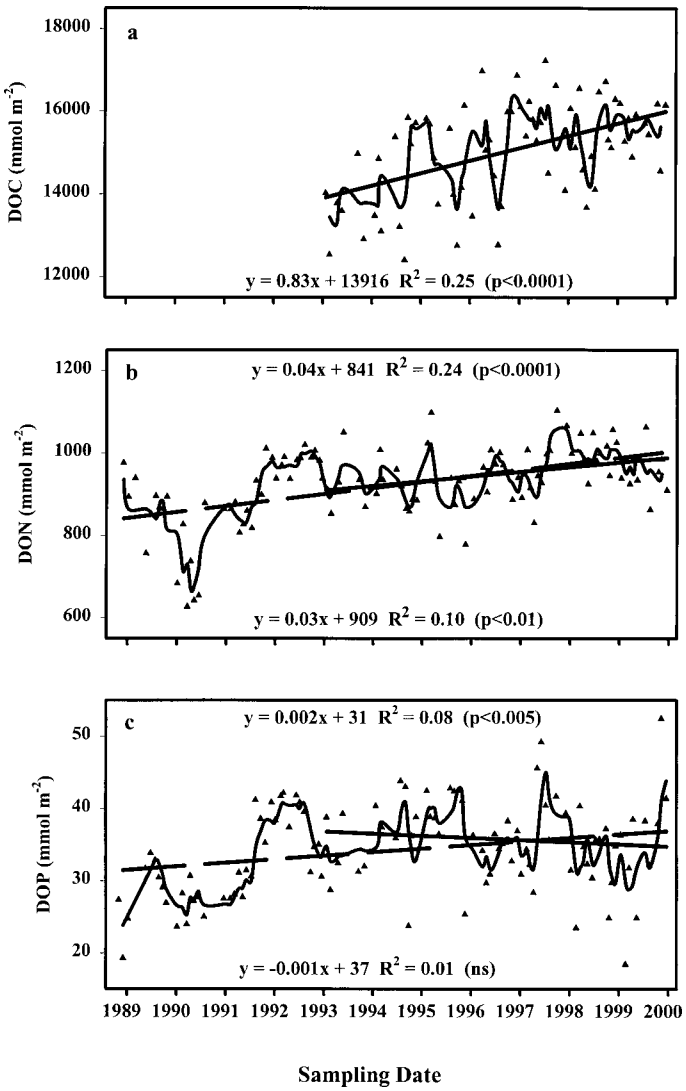



Fig. 4. EZ (0–175 m) depth-integrated DOM inventories at Station ALOHA. Triangles are integrated inventories from each cruise; solid trend lines represent the three-point running mean of DOM inventories. (a) Dissolved organic carbon; solid line is the least squares Model 1 linear regression of cruise data (1993–1999). Equation describing least-squares linear regression (1993–1999) is shown on bottom of panel; x is days since 1 January 1993. (b) Dissolved organic nitrogen; solid line is Model 1 linear regression of data (1993–1999) and dashed line is Model 1 linear regression of data (1989–1999). Equation on the top of panel describes the regression line for the 1989–1999 period; equation shown on the bottom of the panel describes the 1993–1999 time period. In both equations, x is days since the beginning of the time series: 1 January 1989 (top equation) or 1 January 1993 (bottom equation). (c) Dissolved organic phosphorus; regression lines and equations are same as above.

ber) by the prokaryotes *Prochlorococcus* and *Synechococcus* (Campbell and Vaulot 1993).

The annual integrated rates of primary production were not significantly different ($P > 0.05$, one-way ANOVA) between 1989 and 1999, with a mean value of 40 mmol C $m^{-2}$ $d^{-1}$ (Table 1). Interannual variability in primary production rates ranged between ~30 and 45 mmol C $m^{-2}$ $d^{-1}$, similar in magnitude to seasonal variability. Chl *a* concentrations always showed a subsurface peak between 100 and 120 m, with integrated EZ inventories ranging between ~17 and 26 mg Chl *a* $m^{-2}$ (Table 1). Heterotrophic bacterial abundance displayed no significant interannual or seasonal differences ($P > 0.05$, one-way ANOVA) (Table 2).

Concentrations of DOM in the upper 175 m of the water column were highest in the upper 50 m (DOC = 85–105 $\mu$M, DON = 4.5–6.2 $\mu$M, DOP = 0.15–0.27 $\mu$M), decreasing through the lower portion of the EZ (DOC = 63–93 $\mu$M, DON 3.7–6.1 $\mu$M, DOP = 0.10–0.25 $\mu$M) (Fig. 2). The mean concentration (i.e., standing inventories divided by 175

m) of DOC in the EZ varied between ~71 and 98 $\mu$M, whereas DON and DOP ranged between 3.6 and 6.5 $\mu$M and 0.11 and 0.30 $\mu$M, respectively (Fig. 3, Table 2).

*Seasonal and interannual variability*—Integrated inventories of DOM displayed significant variability and several consistent long-term trends (Figs. 3, 4; Table 2). DOC, DON, and DOP inventories fluctuated by as much as 30% on an annual basis (Figs. 2–4); however, no significant seasonal differences were observed (one-way ANOVA, $P > 0.05$, Fig. 3). From 1993 to 1999, integrated DOC concentrations in the upper 175 m of the water systematically increased at a rate of 303 mmol C $yr^{-1}$, resulting in a ~14% net increase in EZ DOC inventories and increasing the mean DOC concentration from ~78 to 89 $\mu$M (Figs. 3, 4; Table 2). Although DOC inventories accumulated throughout the entire EZ, the relative increases were most dramatic toward the base of the EZ (Fig. 2). For example, the mean concentration of DOC at the base of the EZ increased nearly 30% between 1993 and 1999, compared to ~10% increase in the surface waters (Fig. 2).

DON inventories increased significantly ($P < 0.001$) throughout the decade-long period of observations (1989–1999) (Figs. 2, 3c, 4). Consistent with DOC inventories, no significant seasonal differences in DON inventories were observed (one-way ANOVA, $P > 0.05$). Interannual increases in DON inventories led to a 15 mmol N $m^{-2}$ $yr^{-1}$ pooling of DON for the full 11-yr data set and 11 mmol N $m^{-2}$ $yr^{-1}$ accumulation for the 1993–1999 period. This consistent accumulation resulted in an overall increase in the bulk DON inventory of roughly 9% and 3%, respectively (Table 2). The 11-yr mean integral DON inventory was 918 mmol N $m^{-2}$. A sharp decline in DON inventories was observed in 1990 when integrated DON inventories dipped to ~740 mmol N $m^{-2}$, the lowest value during the decade of observations (Fig. 4; Table 2). A substantial increase in DON inventories was observed between 1990 and 1993, increasing inventories from ~740 mmol N $m^{-2}$ to 924 mmol N $m^{-2}$ (Fig. 4; Table 2).

Similar to DOC and DON, DOP inventories displayed no significant seasonal trend (one-way ANOVA, $P > 0.05$). DOP displayed a small increase between 1989 and 1999 at a rate of 0.73 mmol P $m^{-2}$ $yr^{-1}$ (Figs. 3, 4). Similar to DON, the largest increase in DOP inventories occurred between 1990 and 1992 (Figs. 3, 4). However, unlike DOC and DON inventories, DOP inventories remained relatively constant between 1993 and 1999, displaying a slight but insignificant decrease through this period (Figs. 3, 4).

*Variability in DOM stoichiometry*—These systematic temporal changes in DOM inventories were reflected in changes in the stoichiometric ratios of the DOM inventories. The most consistent trend was a significant increase in the DOC : DOP ratio through time (Fig. 4; Table 2). Increases in DOC enriched the bulk DOM pool in C relative to P by ~17% between 1993 and 1999 (Table 2). The bulk DOC : DOP molar ratios increased from 408 to 478 : 1 (Fig. 5; Table 2). DON : DOP molar ratios also showed slight but insignificant increases from 28 : 1 in 1990 to 31 : 1 in 1998, while the bulk DOC : DON molar ratios remained relatively constant, ranging between ~15 : 1 to 16 : 1 (Table 2). Interannual accumulation of DOC and DON also resulted in changes to the C : N : P stoichiometry of the accumulated pools of DOM. The DOC : DON ratio of the accumulated DOM was ~66 : 1, while the DON : DOP ratio of the accumulated DOM was 15 : 1, and the resulting DOC : DOP ratio was 992 : 1.

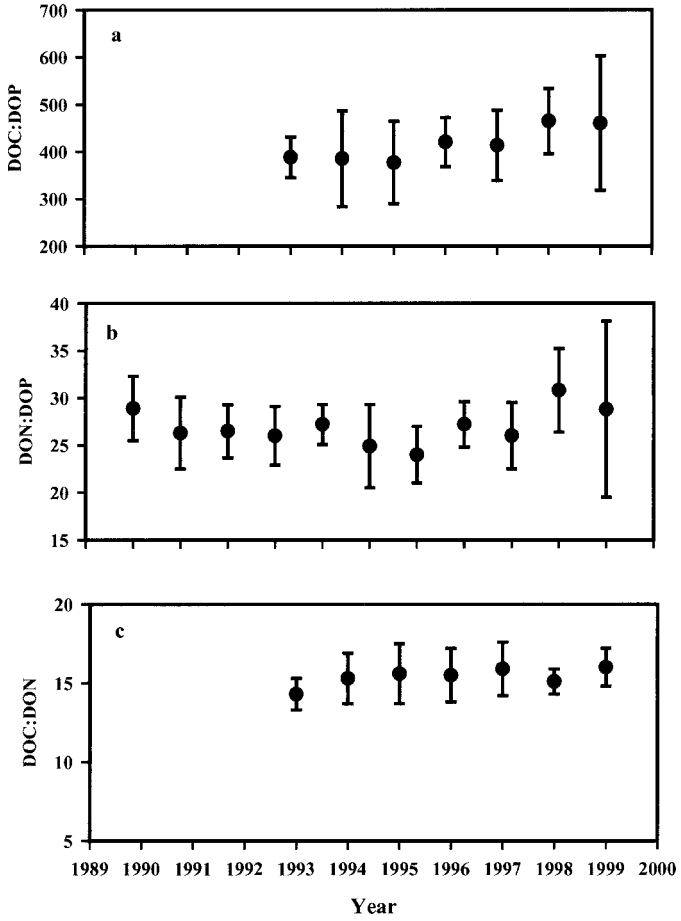



Fig. 5. Interannual changes in the EZ DOM stoichiometry. (a) DOC : DON, (b) DOC : DOP, and (c) DON : DOP molar ratios of DOM inventories. Solid circles represents mean ratio and error bars are standard deviation of the mean for each year presented. No DOC data available for the initial period of observation (1989–1992).

## Discussion

*DOM cycling in the NPSG*—Examining temporal variability in bulk DOM inventories has broad importance for our understanding of ocean biogeochemistry and microbial ecology. Temporal changes in the elemental composition of bulk DOM reflect alterations in the rates of production or utilization of organic matter in the marine environment. Our observations support previous studies suggesting that the NPSG has undergone fundamental changes in the past decade (Karl 1999; Karl et al. 2001*a*). In particular, we maintain that multiyear variability in DOM inventories implies that between 1989 and 1999, the NPSG was undergoing ecologically and biogeochemically important transitions. We argue that these transitions may reflect the response of the

planktonic community to enhanced nitrogen fixation and shifting phototrophic community composition.

Between 1993 and 1999 we observed a significant accumulation of DOC and DON with no corresponding increase in DOP. The resulting DOC : DOP and DON : DOP molar ratios of the bulk DOM were 478 : 1 and 29 : 1, respectively. Total net accumulation of DOC for the 7-yr period between 1993 and 1999 was ~2,100 mmol C $m^{-2}$, resulting in more than an 12-$\mu$M increase in DOC concentrations over the entire EZ (Figs. 2–4; Table 2). The concentration of DON increased at 15 mmol N $m^{-2}$ $yr^{-1}$, for a mean net increase of more than ~165 mmol $m^{-2}$ over the 11-yr period (Fig. 4). The net accumulation of a C- and N-enriched DOM pool implies non–steady state dynamics in production and utilization of organic matter in the surface ocean.

Studies examining DOC production in the NPSG indicate that exudation of photosynthetically produced carbon may account for as much as 50% of the gross primary productivity of the NPSG (Karl et al. 1998). The high DOC production rates estimated from the NPSG may result from several factors acting individually or in concert. First, the predominance of small prokaryotes in the surface-water phototrophic communities may result in high DOM production rates (Bjørnsen 1988; Hagström et al. 1988; Jumars et al. 1989). Second, DOM production due to nitrogen-fixing microorganisms may account for a portion of the accumulated DOM because both C- and N-rich DOM accumulated (Capone et al. 1994; Gilbert and Bronk 1994). Finally, diminishing inventories of bioavailable P could enhance DOM production while decreasing DOC and DON utilization. Based on our analysis of DOM cycling in the NPSG, the processes governing accumulation of DOC and DON appear to operate over multiyear time scales. A tight seasonal coupling between DOM production and consumption appears superimposed over small (<1% of gross primary production) but significant secular accumulations of DOC and DON. Apparently, the microbial processes responsible for DOM cycling over annual time scales are retentive with respect to DOP and relatively nonconservative with respect to DOC and DON. The net result of these processes is the build-up of C- and N-rich DOM over annual to decadal time scales.

Karl et al. (1997) observed significant changes in the dissolved and particulate N and P inventories at Station ALOHA between 1989 and 1994, a finding they attribute to enhanced nitrogen fixation. These authors described multiyear increases in DON inventories accompanied by decreases in SRP inventories. Coincident with these trends, Karl et al. (1997) noted increases in DOP inventories, hypothesizing that these increases were due to an enhanced production of biorefractory DOP. Our analyses support Karl et al. (1997), with one exception: toward the latter half of our observation period (1993–1999), integrated DOP inventories remained unchanged. The observed decrease in the rate of DOP accumulation may reflect increased biological demand for P over time and enhanced retention of P by the biota. In support of these observations, P-limited plankton growth is hypothesized to temporally uncouple DOC production and its utilization (Thingstad et al. 1997), consistent with our observed accumulations of DOC and DON.

*DOM variability in oligotrophic oceans*—The processes responsible for DOM cycling in oligotrophic oceans have received considerable attention over the past decade. In particular, studies evaluating the temporal dynamics of DOC in the oligotrophic Sargasso Sea and the northwestern Mediterranean (Copin-Montegut and Avril 1993; Carlson et al. 1994; Hansell and Carlson 2001) have revealed an important seasonal dynamic in DOC inventories. The cyclic interaction between stratification of sea surface waters and increased vernal primary production appears to drive seasonal DOC dynamics in the surface waters of these seasonally variable regimes. Such studies indicated that DOC production and export represent a potentially important permutation of the biological pump in oligotrophic environments (Ducklow et al. 1995).

No consistent pattern of seasonal production and removal of DOC was observed during the 11 yr of our study at Station ALOHA. Instead, a multiyear net accumulation of DOC and DON throughout the upper ocean was observed. The seasonally driven process of DOC accumulation observed in the surface waters of the Sargasso and Mediterranean Seas apparently manifests itself over interannual and subdecadal time scales in the NPSG. The lack of seasonal mixing in surface waters at Station ALOHA results in diffusion-dominated export of DOM rather than the seasonal pumping witnessed in other oligotrophic oceans (Copin-Montegut and Avril 1993; Carlson et al. 1994). The resulting long-term accumulation of DOM reflects multiyear excesses in the balance between production, utilization, and diffusive loss, rather than the seasonal-scale imbalances observed in other oligotrophic oceans.

In their study of temporal DOC dynamics in the oligotrophic Sargasso Sea, Carlson et al. (1994) observed net seasonal mixed-layer accumulations of DOC of ~1.2 mol C $m^{-2}$. Of this DOC input, approximately 10% turned over on seasonal time scales, and the remaining ~90% was exported to depth with winter convective mixing (Carlson et al. 1994). Similarly, Copin-Montegut and Avril (1993) estimated that ~1.5 mol C $m^{-2}$ of the annually produced DOC in the Mediterranean Sea was seasonally exported from the surface ocean. Our analyses indicate net annual accumulation of DOC in the surface NPSG equals ~0.3 mol C $m^{-2}$, approximately 20% of the amount of DOC annually exported in the Sargasso and the Mediterranean Seas. Moreover, the long-term accumulation of DOC in the EZ was nearly 30% as large as estimated total carbon export from this system (Emerson et al. 1997).

The mean rate of net $^{14}C$ incorporation into particulate matter in the EZ at Station ALOHA for the 1993–1999 period was 40 mmol C $m^{-2}$ $d^{-1}$ or ~15 mol C $m^{-2}$ annually. Balancing this estimate of net primary production with our estimate of net DOC accumulation of ~0.3 mol C $m^{-2}$ $yr^{-1}$ and calculated total export rates of approximately 1 mol C $m^{-2}$ $yr^{-1}$ (Emerson et al. 1997) indicates that 91% of the net primary production was remineralized in the EZ. The remaining 9% of this net production was exported (7%) below the 175-m depth horizon or cycled on time scales greater than 1 yr and accumulated in the EZ (2%). If DOC production rates in the NPSG approximate particle production rates (Karl et al. 1998), gross production in the NPSG could be

as high as 30 mol C $m^{-2}$ $yr^{-1}$. Given this scenario, >95% of the gross primary production would remineralized in the EZ, leaving ~1% of this production to accumulate as DOC.

The apparent net rise in DON inventories between 1988 and 1999 was one of the most intriguing observations in this study. Assuming the 15 mol C $m^{-2}$ measured as the mean annual $^{14}C$ production rate had a C : N molar ratio approximating Redfield stoichiometry of 6.6 : 1, our estimate of annual nitrogen-based primary production was ~2.0 mol N $m^{-2}$ with N export below the EZ exceeding 0.15 mol N $m^{-2}$ $yr^{-1}$. Balancing this production and export with our calculated rise in DON inventories (0.01 mol N $m^{-2}$ $yr^{-1}$) indicates that 92% of the annually produced organic N was remineralized in the EZ. The remaining 8% of this DON was exported (7.5%) or cycled on time scales greater than 1 yr and accumulated in the EZ (0.5%). Based on examination of the dynamics of the DOM inventories at Station ALOHA, it appears that a large fraction (>90%) of the annually produced DOM turns over on short time scales (<1 yr), while a small fraction (~1%) of unutilized DOM grows progressively richer in C and N relative to P and may escape degradation altogether.

*Climate change and biogeochemical implications*—Changes in the DOM inventories at Station ALOHA may be a reflection of changes in the plankton community structure driven by basin-scale climate variability. Investigations on surface-water chemistry, physics, and biology of the North Pacific have emphasized the coherence of upper ocean processes with interannual- and decadal-scale climate variability (Karl et al 1997; McGowan et al. 1998; Karl 1999; Karl et al. 2001*a*,*b*). Modification of surface-water circulation and enhanced stratification may have reduced the frequency of deep mixing events in the NPSG. Such changes have been attributed to the occurrence and duration of El Niño Southern Oscillation (ENSO) events (Karl 1999). The lack of surface-water mixing events that penetrate into the permanent nutricline restricts the delivery of new nutrients into the surface ocean and maintains the oligotrophic character of the gyre.

The non–steady state changes in bulk DOM inventories significantly altered the underlying elemental stoichiometry of the bulk DOM inventories. Between 1993 and 1999, the average C : N : P signature of bulk DOM inventories at Station ALOHA increased from ~408 : 28 : 1 to 478 : 29 : 1 (Fig. 5). The DOC : DON ratio of the bulk DOM pool was more than two times greater than the Redfield ratio of 106 : 16, and the resulting DOC : DOP ratio was more than four times richer in C relative to the Redfield ratio. Between 1993 and 1999 the bulk DON : DOP ratio grew ~7% while the bulk DOC : DOP ratio increased by 16% (Fig. 5). More importantly, the resulting C : N : P ratio of the accumulated DOM was 992 : 15 : 1, approximately 10 times richer in C relative to the Redfield ratio. We are unaware of any other study documenting a systematic change in the bulk oceanic DOM C : N : P ratios over multiyear time scales. Increases in the C : N : P stoichiometry of the bulk DOM suggest either that inputs of C- and N-rich organic matter accelerated during this period or that selective heterotrophic utilization of P-rich compounds became more prevalent.

Accumulations of C- and N-enriched DOM relative to P are important to quantify for complete understanding of biogeochemical cycling in the world's oceans. If C- and N-rich DOM accumulate under conditions favoring nitrogen fixation, revision of our understanding of carbon transport to the deep ocean in oligotrophic systems may be required. New production defines the process whereby the removal of particulate and dissolved material from the surface ocean is balanced by input of new nitrogen into the surface ocean (Dugdale and Goering 1967; Eppley and Peterson 1979). If the observed DOM production and utilization imbalances are fueled by nitrogen fixation, then new nitrogen input may not be temporally coupled to vertical export of carbon. The near-surface accumulation of C- and N-rich DOM comprises an alternative pathway to vertical export for multiyear carbon storage. Considered together, such near-surface C and N pooling may require reconsideration of the NPSG's capacity for carbon storage. Unlike the seasonal accumulation and export of DOM witnessed in the oligotrophic Sargasso and Mediterranean Seas, the EZ of the NPSG appears to focus DOM dynamics on interannual to interdecadal time scales. Such behavior reflects multiyear production imbalances and reflects the NPSG capacity for subdecadal C and N DOM storage in the upper water column.

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