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Seasonal, interannual and decadal variations in particulate matter concentrations and composition in the subtropical North Pacific Ocean

Dale V. Hebel, David M. Karl*

Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822, USA

Abstract

The mean distributions of particulate carbon (PC), nitrogen (PN) and phosphorus (PP) in the euphotic zone (EZ) at Sta. ALOHA (22°45′N, 158°W) in the North Pacific Subtropical Gyre (NPSG) reveal a two-layered system with distinct upper (0–75 m) and lower (75–175 m) EZ dynamics. Particulate matter mean concentrations in the upper EZ were relatively constant with depth, and those in the lower EZ decreased significantly with increasing water depth. The vertical partitioning of particulate matter was approximately 60% in the upper EZ and 40% in the lower EZ. Significant temporal variability, both seasonal and interannual, was observed within both regions. PC and PN inventories in the upper EZ displayed a distinct annual cycle with variable interannual amplitude. The annual cycle was characterized by PC and PN maxima in summer and fall, and minima in winter. PP exhibited a smaller variation with season but also had a distinct wintertime minimum. These variations in particulate matter concentrations were accompanied by seasonal changes in elemental composition; summer and fall conditions were characterized by high C : P and N : P ratios exceeding 140 : 1 and 20 : 1, respectively. It is hypothesized that these concentration and composition patterns result from a net seasonal accumulation of non-living particulate matter throughout the summer and fall periods, and a rapid export during transition to winter conditions. Data also suggest that PN inventories in the NPSG have increased during the past three decades in response to changes in habitat, community composition or both. These temporally decoupled seasonal, interannual and decadal-scale ecological processes will complicate attempts to achieve mass balance or to derive mechanistic biogeochemical models. © 2001 Elsevier Science Ltd. All rights reserved.

* Corresponding author. Tel.: + 1-808-956-8964; fax: + 1-808-956-5059.
E-mail address: dkarl@soest.hawaii.edu (D.M. Karl).

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1. Introduction

Particulate matter plays a vital role in major biogeochemical cycles of many elements and compounds in the marine environment. Although particles can be transported to the sea by riverine and atmospheric processes, the majority of particles is formed by in situ processes either directly or indirectly as a result of biological activity (Karl et al., 1991). However, despite the crucial role of living organisms in the formation and maintenance of particles, the living fraction is generally less than half of the total particulate organic matter pool. The remainder has been termed particulate organic detritus (Odum and de la Cruz, 1963). The non-living organic matter pool takes three major forms: dissolved, colloidal, and "particulate". Colloidal organic carbon (approximately 1 nm–1 μm), the size class that falls between the more well-characterized "dissolved" and "particulate" pools, is actually the largest particulate matter reservoir in the sea (Koike et al., 1990; Wells and Goldberg, 1991; Kepkay, 1994).

Once formed particles may sink, rise, aggregate/disaggregate, dissolve or be transformed or consumed by other particles. These multiple sources, sinks and interactions predict the existence of a diverse and variable particle spectrum in most marine habitats. Consequently, the distribution, abundance and characterizations (e.g., morphological, chemical, mineralogical, biological and optical) of the marine particulate matter pools are crucial for many otherwise unrelated subdisciplines of oceanography (Fowler and Knauer, 1986; Hurd and Spencer, 1991), including contemporary topics such as global ocean fluxes and oceanic sequestration of atmospheric carbon dioxide (Longhurst, 1991).

The ambient concentration of particulate matter at any given location represents the balance between production (or supply) and remineralization (or removal) processes. While these static inventories by themselves cannot be used to estimate fluxes or to model the response of habitat change, particulate-matter determinations are necessary for understanding both regional and global biogeochemical cycles.

Pioneering research efforts on the global distributions of particulate matter conducted nearly three decades ago provided a coherent view of regional and depth-dependent variations of particulate carbon (PC) and associated bioelements (summarized in Riley, 1970; Menzel, 1974; Parsons, 1975). Based largely on these data sets, it was established that the concentration of particulate matter decreased with distance from shore and with depth at a given location. The most consistent interpretation was that these patterns were sustained by variations in primary production and ultimately by the large-scale circulation features of the global ocean.

More modern methods of analysis, which include ^{14}C-based ($\Delta^{14}C$) age dating of particulate matter in seawater, have suggested a much more complex control, with large seasonal and interannual variations in particulate matter (reported as particulate organic carbon, POC) concentration, composition and apparent age (Druffel et al., 1996). Among the most noteworthy features were (Druffel et al., 1996): (1) large differences in the mean ages of various carbon pools (dissolved, "suspended" POC and "sinking" POC); (2) the large depth variations in "suspended" POC age with youngest particles at the surface, and (3) the extremely large temporal variations in the apparent age of the "sinking" particles ($\Delta^{14}C$ range from $+154‰$ in Oct 1991 to $-21‰$ in Dec 1991 for sediment–trap-collected particles). The authors attributed the latter, unexpected, results to a complex interaction between relatively young rapidly sinking POC and very old (>6000 years

before present) dissolved organic carbon (DOC). These potential DOC–POC interactions re-emphasize the complexities mentioned above for oceanic carbon cycle processes.

Subtropical ocean gyres occupy about 40% of the earth's surface, but particulate-matter dynamics in these regions remain poorly described relative to the more accessible neritic and coastal zones. The North Pacific Subtropical Gyre (NPSG) is the largest of these open-ocean regions and as such represents the largest biome on our planet. In terms of their inherent optical properties, including both light absorption and light scattering, these open-ocean regions have been termed "case 1" waters (Jerlov, 1951; Morel and Prieur, 1977). Bishop (1999) has recently demonstrated that the beam attenuation coefficient at 660 nm, measured using a submersible transmissometer, can be used to make continuous and potentially unattended estimates of POC in diverse marine environments. With the advent of satellite-based remote-sensing technologies, the sea surface characteristics of expansive regions can now be studied on near-synoptic time scales (Yoder et al., 1993), and it has recently been reported that POC can be estimated from orbiting satellites by analyzing optical backscattering characteristics (Stramski et al., 1999). These diverse data sets have revealed heterogeneity on multiple time and space scales. These variations had not been appreciated on the basis of data collected from ship-based oceanographic expeditions. Furthermore, data collected at the Hawaii Ocean Time-series (HOT) Sta. ALOHA in the NPSG have documented seasonality in the deep chlorophyll maximum layer (Letelier et al., 1993), the depth of nitracline (Dore and Karl, 1996), temperature, salinity and dissolved oxygen (Bingham and Lukas, 1996), in situ fluorescence and chl *a* (Letelier et al., 1993; Winn et al., 1995), picoplankton abundance (Campbell et al., 1997) and rates of primary production (Karl et al., 1998), so it is possible that particulate-matter inventories also might reveal temporal change.

This paper presents observations of particulate carbon (PC), nitrogen (PN) and phosphorus (PP) at the HOT program Sta. ALOHA for the period Oct 1988–Dec 1997. Companion papers (Karl et al., 2001a, b) present dissolved organic and inorganic nutrient dynamics and long-term trends in plankton community structure. The particulate-matter observations reveal a robust annual cycle in the upper euphotic zone (EZ) with maxima in late summer and minima in winter, but with variable interannual amplitudes. These temporal dynamics correspond to an overproduction of particulate matter, relative to removal rates, in spring and summer seasons followed by a period of net particulate-matter removal in fall. We also compare our data to similar time-series measurements of PC and PN reported by Gordon (1970, 1971) for the period 1969–1970, and present an hypothesis to accommodate the decadal changes in PC and, especially, PN inventories that are observed for this region of the world ocean.

2. Materials and methods

2.1. Station location, sample collections and PC/PN/PP analyses

Water samples were obtained at Sta. ALOHA (22°45′N, 158°00′W; Fig. 1) on approximately monthly intervals from the period Oct 1988–Dec 1997. Seawater was collected using a 24-place rosette sampler configured with a Sea-Bird 911-plus CTD (Karl and Lukas, 1996). Typically, 8–14 depths were sampled from the surface to 1000 m with the majority of samples collected in the upper

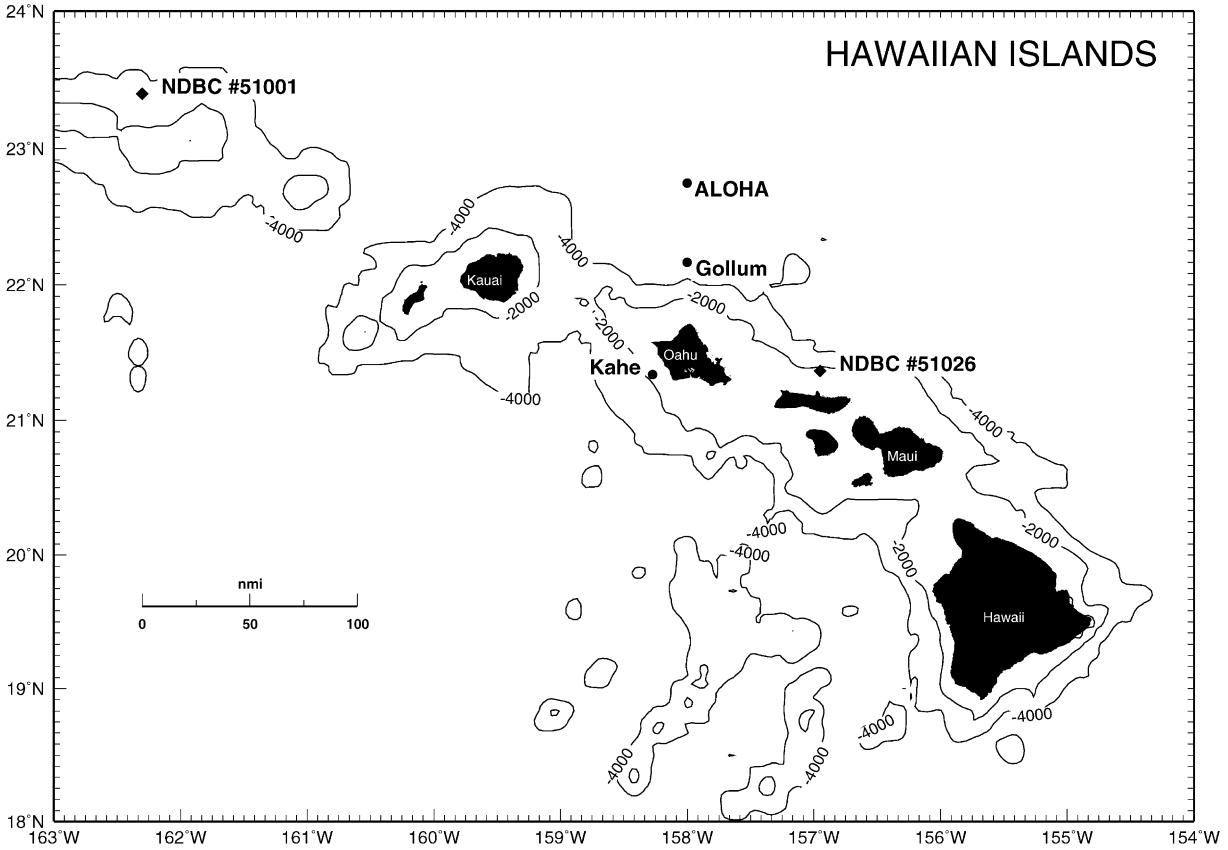


Fig. 1. Map of a portion of the North Pacific Subtropical Gyre showing the location of Sta. ALOHA (22°45′N , 158°W) where this study was conducted. Sta. Gollum (22°10′N , 158°W), the site of a 1969–1970 time-series sampling study Sta. Kahe (the HOT coastal site), and two NDBC moorings (# S1001 and #S1026) are also shown. Contours are water depth in meters.

200 m and corresponding to the depths used to measure primary production, pigments and other related core parameters (5, 25, 45, 75, 100, 125, 150 and 175 m). Replicate samples were routinely collected from a single water bottle and periodically from paired water bottles tripped at the same depth on the same cast (i.e., field replicates). Sample volumes used for PC and PN determinations ranged from 4-l per sample for depths $\leqslant 150$ m to 10-l per sample for depths > 150 m. Subsamples were transferred into acid-cleaned polyethylene aspirator bottles via Tygon® tubing with a 202 μm Nitex® screen to exclude large particles, including mesozooplankton. The bottles and tubes were rinsed three times each with water from the pre-determined depth before collection of the final sample used for analysis. The entire contents of each aspirator bottle was pressure filtered (4–7 psi N_2 gas) through combusted (450°C, 4 h) glass fiber filters (Whatman GF/F, 25 mm diameter) contained in a Delrin in-line filter holder with stainless-steel screen base. Following this procedure the particle-loaded filter was placed onto a 2.5 cm^2 combusted aluminum foil contained in a plastic Petri dish and stored frozen (-20°C) until analyzed. Prior to analysis the filters were dried at 50–60°C for 24 h.

PC and PN were both measured from a common filter using a commercially available high-temperature combustion CN analyzer (Hewlett-Packard model 185 analyzer for HOT-1 to HOT-6; Perkin Elmer model 2400 analyzer for HOT-7 to HOT-53; Europa Scientific SL analyzer for HOT-54 to HOT-88), as described by Karl et al. (1991). The coefficient of variation for field replicated PC and PN samples averaged 12 and 10%, respectively, for the elemental masses typically measured in this study. Primary PC/PN standards were prepared using acetanilide (C_8H_9NO; molecular weight = 135.16). The overall accuracy, expressed as the mean difference between the acetanilide standard, was 6% for C and 13% for N. A secondary, pulverized plankton standard prepared for use in the HOT program also was analyzed as an "unknown" sample to track the long-term reproducibility of this analysis. During the 9-yr period of investigation the secondary standard had a relatively stable C:N molar ratio (mean = 5.0, se = 0.2, $n = 83$). Combusted but otherwise untreated GF/F filters were used as sample blanks. PC and PN blanks averaged 1 μmol C and 0.01 μmol N, respectively, compared to water samples containing approximately 4–8 μmol C and 0.4–1.5 μmol N per filter.

Particulate phosphorus (PP) samples were collected and subsampled as described above, except that the combusted GF/F filters were HCl-rinsed before use to further reduce the P blank. Sample volumes ranged from 4-l for water depths $\leqslant 150$ m to 10-l for greater depths. Following filtration the GF/F filters were placed in combusted, acid-rinsed 12×70-mm glass test tubes, covered with foil and stored frozen. In the shore-based laboratory the PP samples were combusted at 475–500°C for 3 h, acid hydrolyzed (HCl, 0.5 M) for 90 min at 80–90°C, centrifuged (2800 *g*, 30 min), and a 5-ml subsample of the supernatent analyzed for soluble reactive phosphorus (SRP) by acid molybdate spectrophotometry (Strickland and Parsons, 1972). Accuracy was assessed from the analysis of a known dry weight of the above-mentioned pulverized plankton standard and from certified reference material (National Institute of Standards and Testing, orchard leaves). The P content of the HOT plankton standard averaged 0.86% (se = 0.02%, $n = 53$) while the orchard leaves with a certified value of 0.20% averaged 0.20% (se = 0.01%, $n = 53$). The coefficient of variation for field replicated PP samples was approximately 15%. Combusted, acid-washed, but otherwise untreated GF/F filters were used as blanks. Blank PP samples averaged 0.64 nmol P per filter compared to water samples containing approximately 20–80 nmol P per filter.

Menzel (1966) suggested that adsorption of dissolved organic matter (DOM) onto glass fiber filters could account for a measurable "blank" in the determination of seawater particulate matter. We have independently determined that DOM recently produced via the process of photosynthesis at Sta. ALOHA is readily adsorbed by glass fiber filters (Karl et al., 1998). Presumably dissolved N and dissolved P compounds also might adsorb albeit with differential efficiencies. This source of error would be depth dependent (greatest at the surface) and would likely increase with decreasing volume processed as a result of filter loading (again, greatest at surface where smaller seawater volumes were filtered). More recently, Moran et al. (1999) have documented a significant interference by dissolved organic carbon (DOC) in quantitative determination of PC from a variety of marine environments. We also have documented a similar effect for samples collected at Sta. ALOHA. This effect would tend to overestimate the ambient particulate-matter concentrations. Additionally, there is the possibility that some sub-micron-sized particles (Taguchi and Laws, 1988; Altabet, 1990; Koike et al., 1990) and most colloids (Wells and Goldberg, 1991) would not be detected by current particulate-matter methodologies. This would tend to underestimate the ambient particulate-matter concentrations. Consequently, and until further improvements in

sampling and subsampling are employed routinely, we should consider our data to represent an operationally defined particulate-matter pool, namely, materials collected using combusted glass fiber filters of 0.7 μm porosity.

2.2. Ancillary HOT data

The CTD-rosette system was used to collect continuous, real-time data on dissolved oxygen concentration, flash fluorescence, temperature, pressure and conductivity. Additional water samples collected from pre-determined depths were analyzed for pigments, dissolved inorganic and organic nutrients, total dissolved inorganic carbon and related properties. These and other core data sets and metadata are available through the World Wide Web at http://hahana.soest.hawaii.edu.

3. Results

3.1. Particulate-matter inventories: concentration versus depth profiles

The 9-yr data set on particulate-matter concentrations at Sta. ALOHA conforms to a priori expectations with maxima in the surface mixed-layers and minima at depth (Figs. 2 and 3). Both seasonal and interannual variations in particulate-matter concentrations are evident, especially in the upper 0–75 m of the water column (Fig. 2). Mean concentrations for the entire data set range from 0.3 to 2.2 μM, 0.04 to 0.33 μM and 1.9 to 16.2 nM for PC, PN and PP, respectively (Fig. 3 and Table 1).

The particulate-matter climatology revealed at least three major zones within the upper 1000 m of the water column (Fig. 3): (1) an upper EZ region (0–75 m) where mean particulate-matter concentrations are high and relatively constant with depth, (2) a lower EZ region (75–175 m) where concentrations decrease rapidly with increasing water depth, and (3) the subeuphotic zone where concentrations are low and decrease only gradually with increasing water depth (250–1000 m). For all three bioelements, the relative partitioning by depth within the EZ was relatively constant in time, with approximately 60% of the total EZ particulate-matter inventory present in the upper EZ and 40% in the lower EZ.

In the lower portion of the EZ (75–175 m) mean PC, PN and PP concentrations all exhibit significant linear decreases with depth (Fig. 3). Based on linear regression analyses of concentration versus depth, the observed PC, PN and PP decreases in the lower EZ are equivalent to 1.35, 0.22 and 0.01 μm/100 m, losses that approximate 60–70% of the 75 m concentrations. The implied C : N : P stoichiometry of these losses is 122C : 20N : 1P, which approximates the dissolved-matter inventories (Karl et al., 2001a).

3.2. Particulate-matter inventories: seasonal to interannual variability

The concentrations of particulate matter display both seasonal and interannual variations, especially within the upper EZ (Figs. 2 and 4–7). Over the 9-yr observation period, a regular seasonal cycle in the standing stocks of PC and PN in the upper EZ is observed (Figs. 4, 5 and 7).

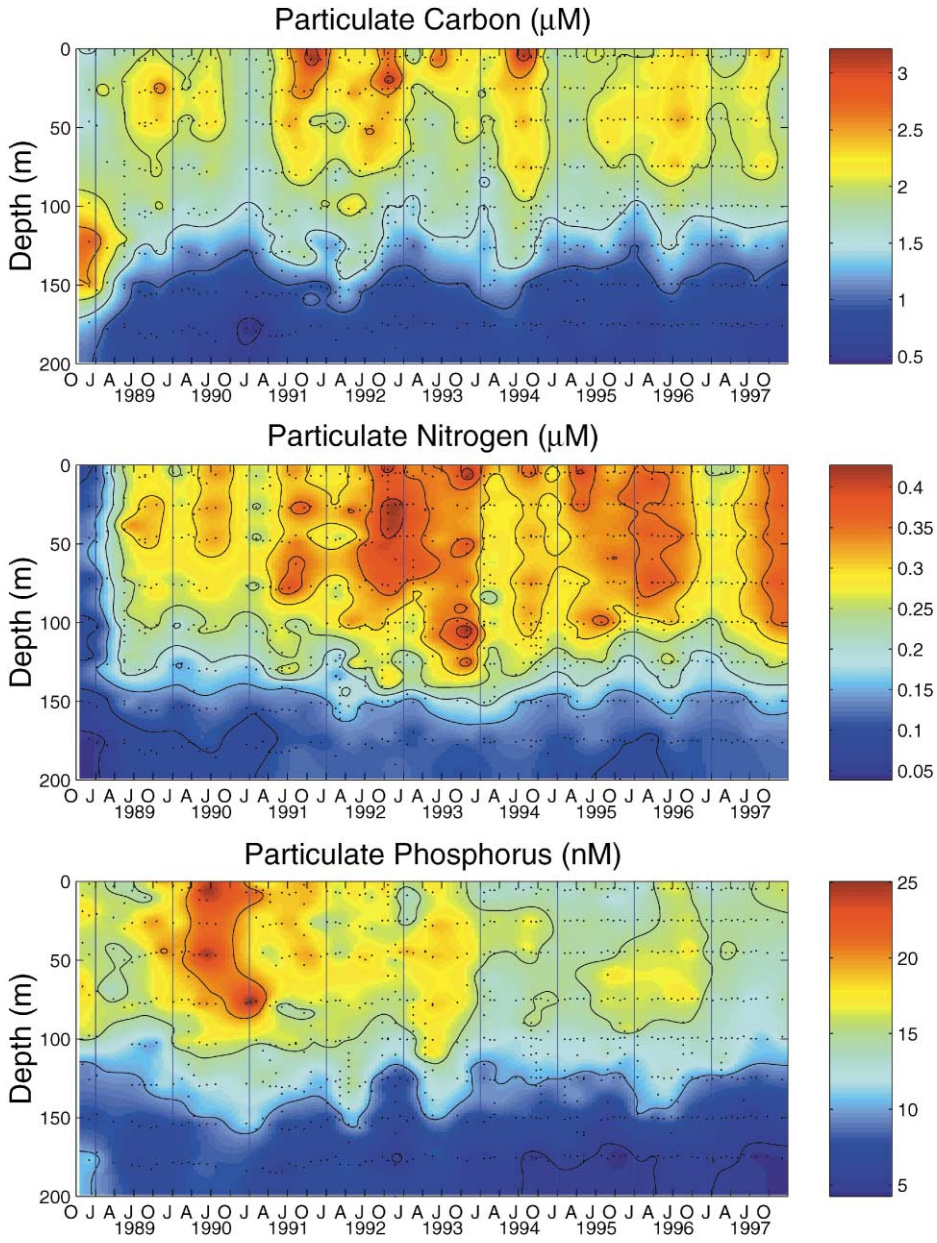


Fig. 2. Concentration versus depth contours for particulate carbon (PC), nitrogen (PN) and phosphorus (PP) concentrations in the upper 200 m of the water column at Sta. ALOHA for the period Oct 1988–Dec 1997. Samples were collected on approximately monthly intervals at the depths indicated by the solid circles. Concentrations are μM for PC and PN and nM for PP.

PC and PN concentrations are lowest in winter, increasing throughout the late spring and summer with concentration maxima in fall (spring is defined as March–May; summer is defined as June–August, fall is defined as September–November, and winter is defined as December–February).

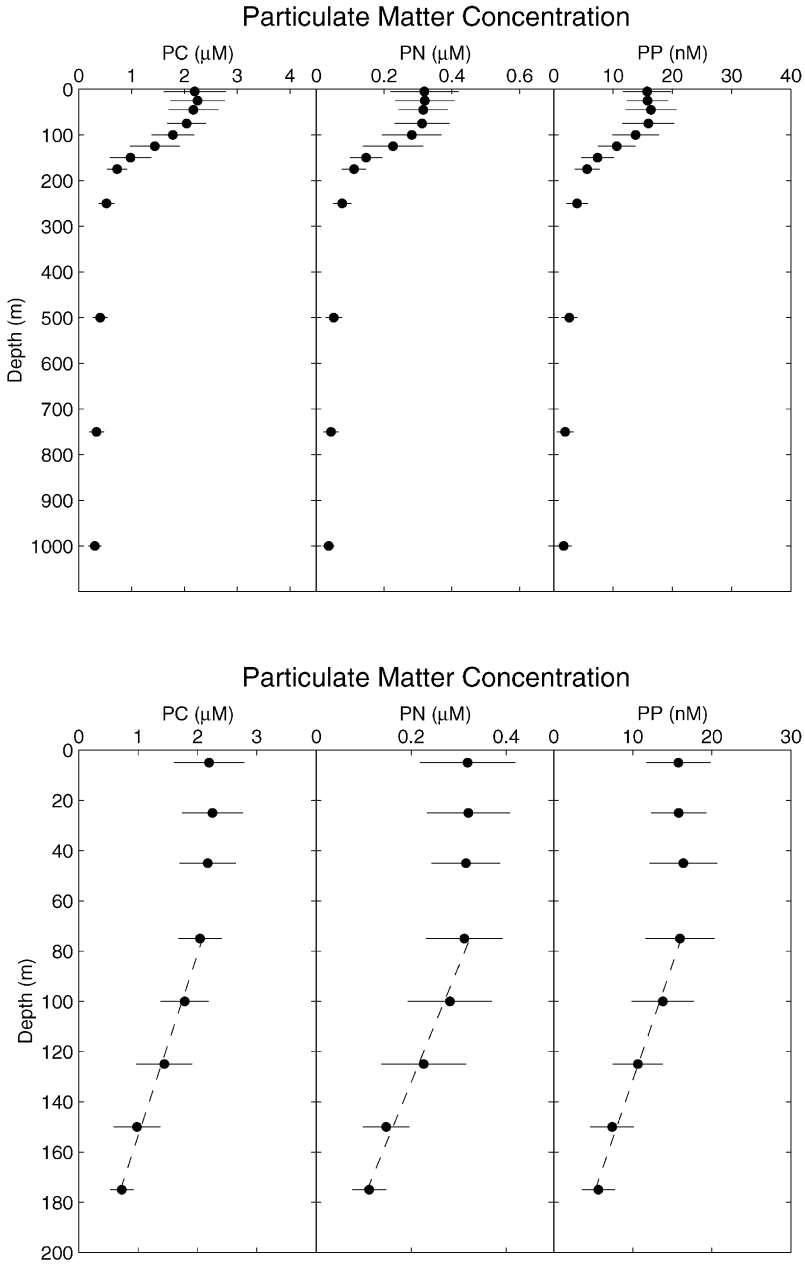


Fig. 3. Concentration versus depth profiles for particulate carbon (PC), nitrogen (PN) and phosphorus (PP) at Sta. ALOHA. [Upper panel]: Mean $\pm$ 1 standard deviation for PC, PN and PP in the upper 1000 m of the water column for the 9-yr data set. [Lower panel]: Mean $\pm$ 1 standard deviation for PC, PN and PP concentration versus depth profiles in the euphotic zone (EZ) only. The dashed lines are model I linear regression fits to the lower EZ (75–175 m) data. The regression statistics are: PC (μM) = (-1.33×10^{-2} μM/m) $\times$ depth (m) + 3.06 μM, $r^2 = 0.990$, PN (μM) = (-2.22×10^{-3} μM/m) $\times$ depth (m) + 0.494 μM, $r^2 = 0.990$, PP (nM) = (-0.111 nM/m) $\times$ depth (m) + 25.0 nM, $r^2 = 0.993$.

Table 1
Particulate matter concentrations and average elemental composition as a function of depth for water samples collected at Sta. ALOHA, Oct 1988–Dec 1997

Depth (m)	Particulate carbon (μM)				Particulate nitrogen (μM)				Particulate phosphorus (nM)				
	Mean median (Range)	SD[a]	SE[a]	*n*	Mean median (Range)	SD	SE	*n*	Mean median (Range)	SD	SE	n	Average PC : PN : PP (molar)
5	2.20 2.04 (1.34–5.12)	0.64	0.07	77	0.325 0.314 (0.063–0.727)	0.110	0.013	77	16.2 15.9 (8.1–32.6)	4.3	0.5	80	136 : 20.1 : 1
25	2.27 2.15 (1.33–4.62)	0.57	0.06	90	0.333 0.321 (0.059–0.806)	0.112	0.012	87	16.5 16.5 (6.8–24.9)	3.4	0.4	78	138 : 20.2 : 1
45	2.12 2.08 (1.16–3.05)	0.40	0.04	81	0.312 0.314 (0.085–0.492)	0.074	0.008	78	17.0 16.9 (10.0–31.7)	4.1	0.5	78	124 : 18.4 : 1
75	2.01 1.99 (1.18–2.96)	0.36	0.04	81	0.317 0.314 (0.019–0.678)	0.090	0.010	82	16.6 16.3 (8.4–35.2)	4.5	0.5	80	121 : 19.1 : 1
100	1.76 1.78 (0.57–2.92)	0.40	0.04	85	0.283 0.286 (0.025–0.657)	0.096	0.010	85	14.2 13.5 (4.8–31.0)	4.1	0.5	83	124 : 19.9 : 1
125	1.41 1.42 (0.63–3.34)	0.45	0.05	77	0.228 0.234 (0.028–0.608)	0.096	0.011	78	10.8 10.5 (4.8–19.4)	3.3	0.4	82	131 : 21.1 : 1
150	0.98 0.87 (0.53–3.14)	0.43	0.05	67	0.144 0.142 (0.018–0.264)	0.048	0.006	67	7.8 7.5 (1.9–15.8)	2.8	0.3	68	126 : 18.5 : 1
175	0.72 0.68 (0.17–1.30)	0.21	0.03	63	0.109 0.104 (0.020–0.207)	0.038	0.005	64	5.9 5.5 (3.3–14.2)	2.1	0.3	68	122 : 18.5 : 1
250	0.53 0.50 (0.10–1.13)	0.14	0.02	73	0.079 0.079 (0.011–0.164)	0.027	0.003	74	4.2 3.9 (2.6–14.9)	1.9	0.2	74	126 : 18.8 : 1
500	0.41 0.38 (0.15–0.90)	0.13	0.02	69	0.055 0.050 (0.007–0.172)	0.026	0.003	70	2.8 2.4 (1.3–8.1)	1.4	0.2	74	146 : 19.6 : 1
750	0.33 0.30 (0.15–0.95)	0.12	0.01	70	0.046 0.043 (0.007–0.150)	0.023	0.003	72	2.2 1.6 (0.6–8.1)	1.5	0.2	71	150 : 20.9 : 1
1000	0.32 0.29 (0.09–0.80)	0.14	0.02	60	0.039 0.036 (0.006–0.079)	0.018	0.002	59	1.9 1.5 (0.6–11.0)	1.5	0.2	60	168 : 20.5 : 1

[a]Standard deviation of the measured mean; SE = standard error of the population mean.

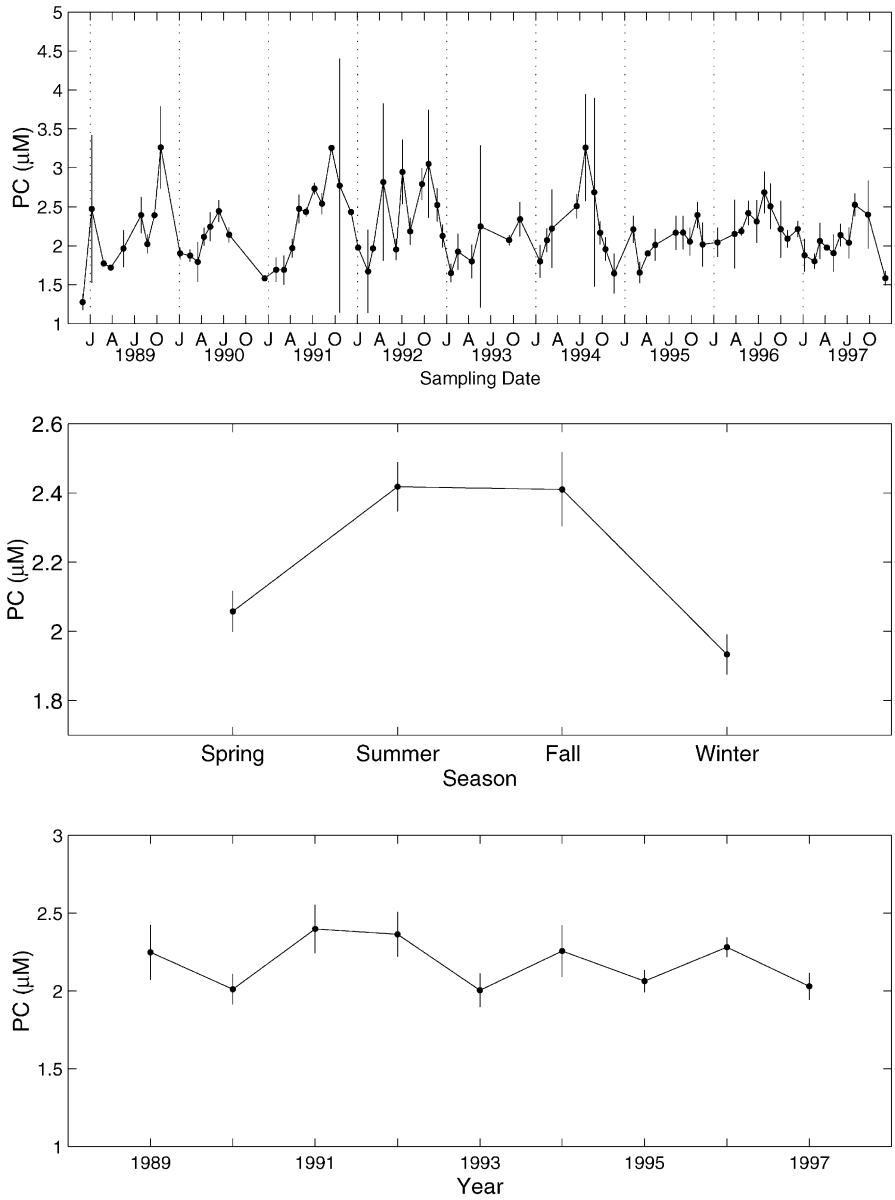


Fig. 4. Monthly, seasonal and interannual variations in particulate carbon (PC) in the upper euphotic zone (EZ) at Sta. ALOHA (0–75 m). Each datum is derived from individual samples collected at 5, 25, 45 and 75 m. [Top panel]: Mean $\pm$ 1 standard deviation PC concentrations versus time from Oct 1988 to Dec 1997. [Center panel]: The 9-yr upper EZ PC data set binned by season and expressed as mean $\pm$ 1 standard deviation where: spring = Mar–May, summer = Jun–Aug, fall = Sept–Nov and winter = Dec–Feb. [Lower panel]: The 9-yr upper EZ PC data set binned by year and expressed as mean $\pm$ 1 standard deviation.

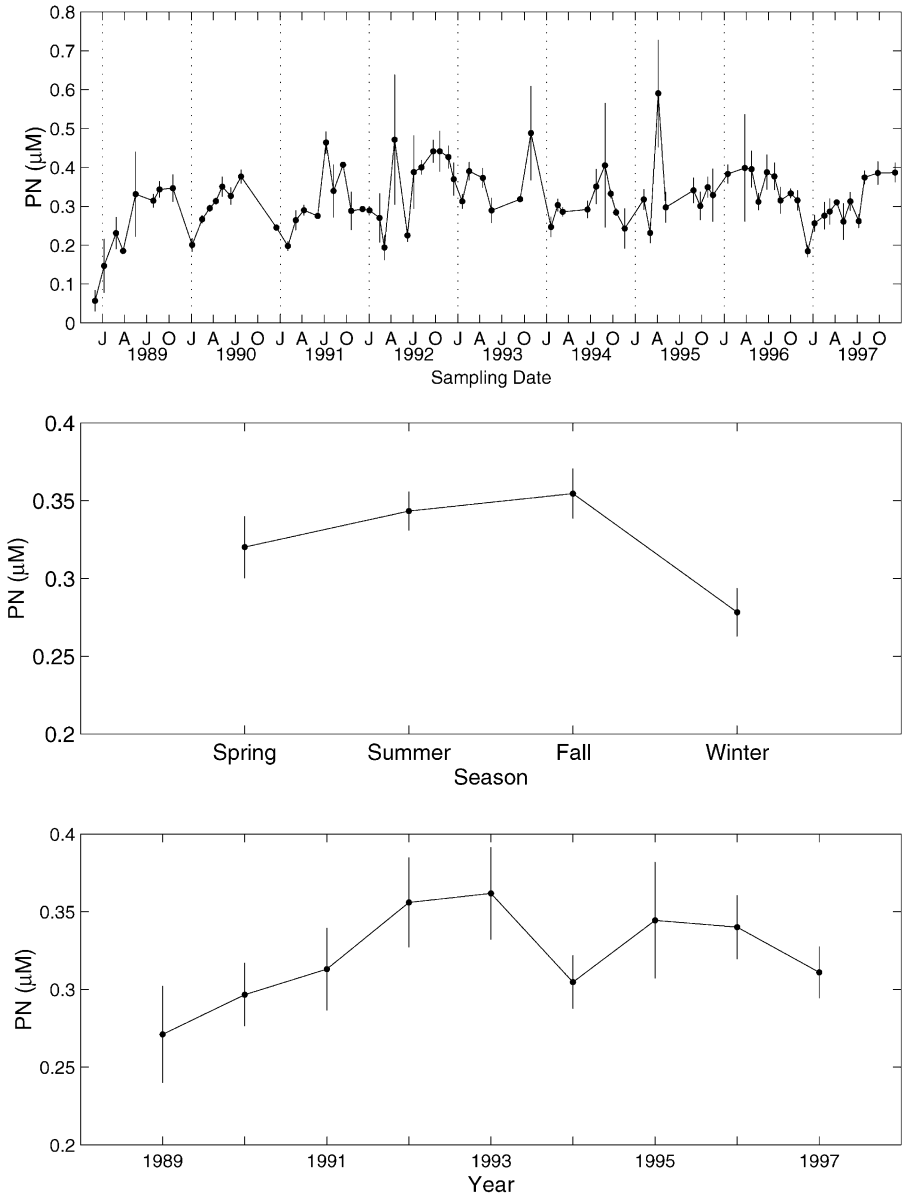


Fig. 5. As in Fig. 4, except for particulate nitrogen (PN).

During the transition from fall to winter, there is a relatively rapid decline back to the annual minimum standing stock of PC and PN (Figs. 4, 5 and 7). These seasonal patterns in the upper EZ also hold for the lower EZ (75–150 m; Fig. 7). In the upper EZ, there was more pronounced interannual variability in PN inventories than there was for PC, with generally increasing concentrations from 1989 to 1993, decreasing thereafter (Fig. 5).

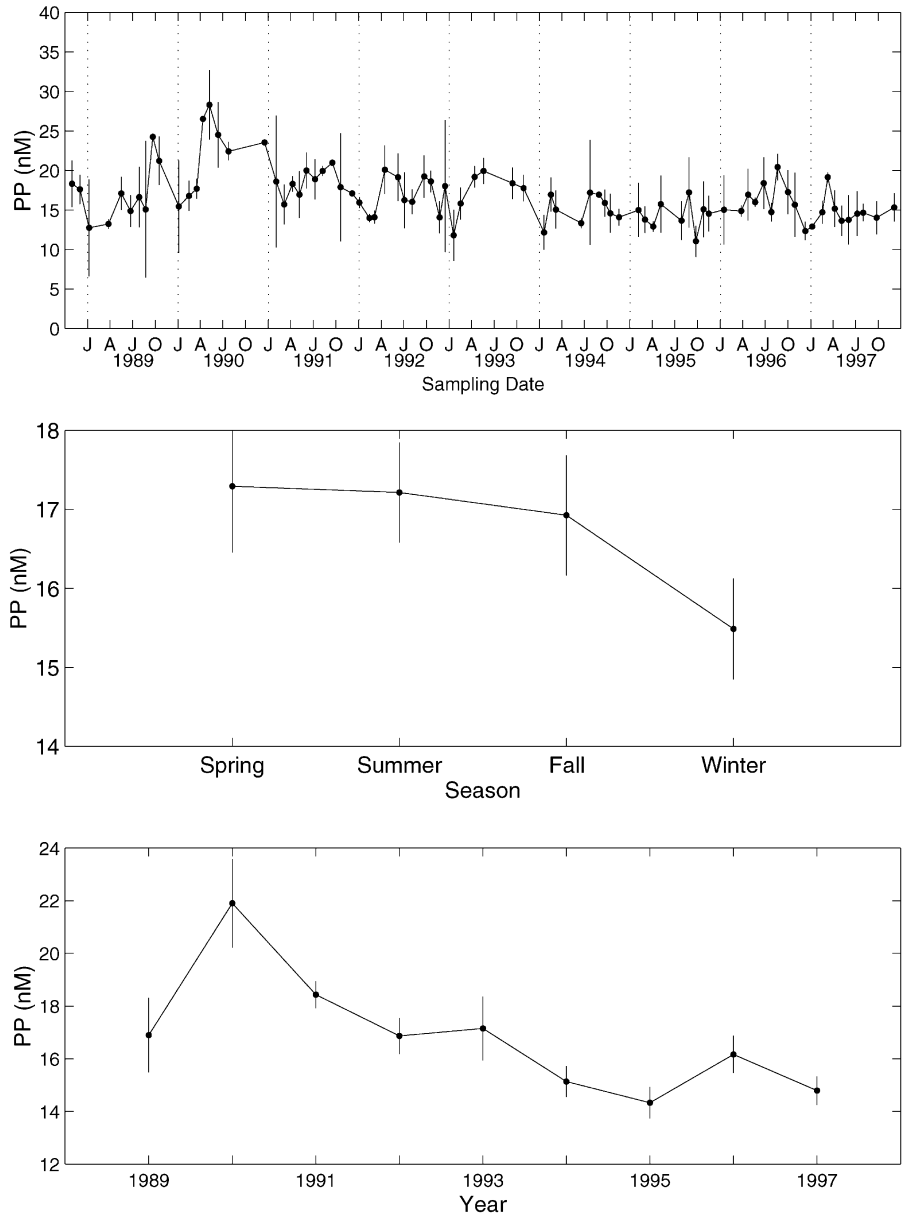


Fig. 6. As in Fig. 4, except for particulate phosphorus (PP).

Seasonality of PP in the upper EZ is less obvious, but springtime maxima and winter minima are still apparent (Figs. 2, 6 and 7). This seasonal pattern was most apparent during the first five years of the program and diminished thereafter (Fig. 6). In contrast to PC and PN, PP in the lower EZ (75–150 m) and in the subeuphotic zone (150–225 m) displayed an opposing seasonal pattern, with highest concentrations in winter and lowest concentrations in fall (Fig. 7). There was also a significant and sustained decrease in the mean 0–75 m PP inventories from 1990 to 1997 (Fig. 6).

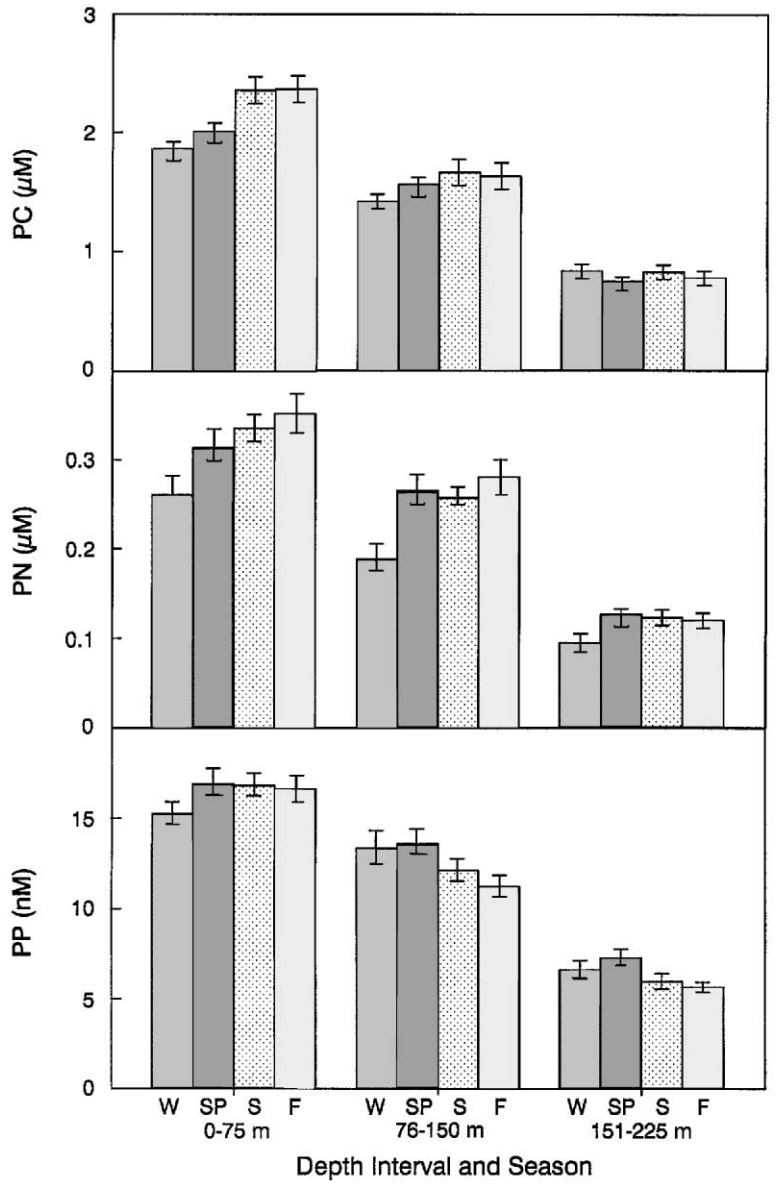


Fig. 7. Variations in the concentrations of particulate carbon (PC), nitrogen (PN) and phosphorus (PP) with depth and season for samples collected at Sta. ALOHA between Oct 1988 and Dec 1997. Data shown are mean ± 1 standard deviation estimates for each respective depth interval and season. Seasons (W = winter, SP = spring, S = summer, F = fall) are defined in Fig. 4.

3.3. Seasonal and interannual variability in stoichiometry of particulate matter

The C : N : P elemental stoichiometry of the particulate matter pools also varied both seasonally and with depth for a given season (Fig. 8; Tables 1 and 2). Although the molar C : N ratio was

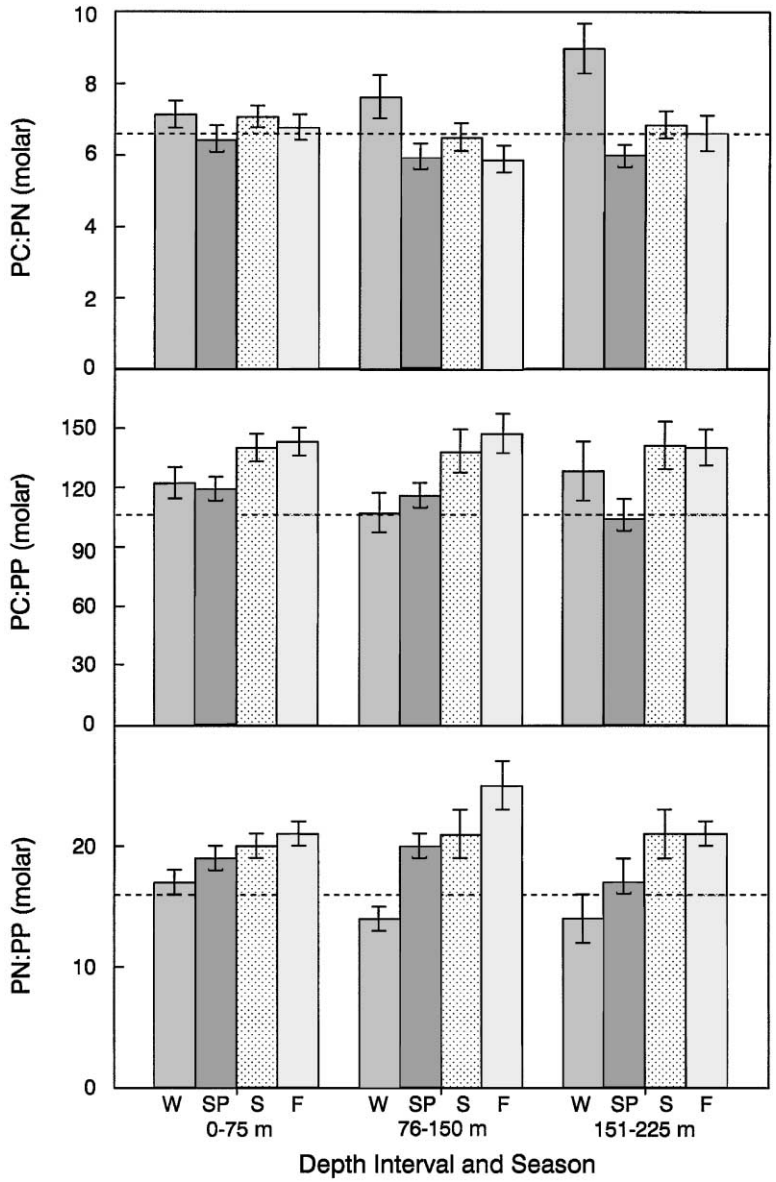


Fig. 8. Variations in the elemental stoichiometry of particulate matter with depth and season for samples collected at Sta. ALOHA between Oct 1988 and Dec 1997. Data shown are the mean $\pm$ 1 standard deviation of the respective molar ratios. Seasons are defined in Figs. 4 and 7.

nearly constant in the upper EZ irrespective of season and was similar in magnitude to the Redfield ratio of 6.6 : 1 (Redfield et al., 1963), both the C : P and N : P ratios increased substantially from winter to fall as particulate matter accumulated (Fig. 8). The summer and fall C : P and N : P molar stoichiometries were significantly greater than the Redfield ratios of 106 : 1 and 16 : 1, respectively.

Table 2
Seasonal variations in particulate carbon (PC), nitrogen (PN) and phosphorus (PP) concentrations and elemental composition for samples collected at Sta. ALOHA from Oct 1988–Dec 1997

Depth interval (m)	Season[a]	PC[b] (μM)	PN[b] (μM)	PP[b] (nM)	PC : PN[c] (molar)	PC : PP[c] (molar)	PN : PP[c] (molar)	Mean PC : PN : PP[d] (molar)
0–75	Winter	1.86 (± 0.06)	0.26 (± 0.02)	15.23 (± 0.62)	7.1 (± 0.4)	122 (± 8)	17 (± 1)	122 : 17.1 : 1
	Spring	2.01 (± 0.07)	0.31 (± 0.02)	16.89 (± 0.84)	6.4 (± 0.4)	119 (± 6)	19 (± 1)	119 : 18.4 : 1
	Summer	2.36 (± 0.11)	0.34 (± 0.01)	16.81 (± 0.63)	7.0 (± 0.3)	140 (± 7)	20 (± 1)	140 : 20.2 : 1
	Fall	2.37 (± 0.11)	0.35 (± 0.02)	16.60 (± 0.73)	6.7 (± 0.4)	143 (± 7)	21 (± 1)	143 : 21.8 : 1
76–150	Winter	1.43 (± 0.06)	0.19 (± 0.01)	13.35 (± 0.95)	7.6 (± 0.6)	107 (± 10)	14 (± 1)	107 : 14.2 : 1
	Spring	1.57 (± 0.06)	0.27 (± 0.02)	13.58 (± 0.81)	5.9 (± 0.4)	116 (± 6)	20 (± 1)	116 : 19.9 : 1
	Summer	1.67 (± 0.11)	0.26 (± 0.01)	12.10 (± 0.61)	6.5 (± 0.4)	138 (± 11)	21 (± 2)	138 : 21.5 : 1
	Fall	1.64 (± 0.11)	0.28 (± 0.02)	11.21 (± 0.59)	5.9 (± 0.4)	147 (± 10)	25 (± 2)	146 : 25.0 : 1
151–225	Winter	0.84 (± 0.06)	0.09 (± 0.01)	6.57 (± 0.49)	9.0 (± 0.7)	128 (± 15)	14 (± 2)	128 : 13.7 : 1
	Spring	0.75 (± 0.04)	0.13 (± 0.01)	7.25 (± 0.49)	6.0 (± 0.3)	104 (± 10)	17 (± 2)	103 : 17.9 : 1
	Summer	0.83 (± 0.06)	0.12 (± 0.01)	5.92 (± 0.42)	6.8 (± 0.4)	141 (± 12)	21 (± 2)	140 : 20.3 : 1
	Fall	0.78 (± 0.06)	0.12 (± 0.01)	5.61 (± 0.27)	6.6 (± 0.5)	140 (± 9)	21 (± 1)	139 : 21.4 : 1

[a]Seasons defined as: Winter (Dec–Feb), Spring (Mar–May), Summer (June–Aug), Fall (Sept–Nov).
[b]Values presented are mean ± 1 standard deviation of pooled measurements from, generally, 4–6 individual determinations in each depth interval.
[c]Values presented are the mean ± 1 standard deviation of the pooled ratios determined for each individual sample in the respective depth interval.
[d]Stoichiometry ratios calculated from the respective depth and season pooled concentration data.

Identical trends with season also were observed in the lower EZ and, for N : P, even at greater depths (Fig. 8).

4. Discussion

A primary goal of the HOT program is to observe and understand the time varying fluxes of carbon and associated bioelements. For nearly a decade, measurements have been made of the standing stocks of PC, PN and PP on approximately monthly intervals. Particulate-matter photoautotrophic production using ^{14}C–HCO_3 and particulate-matter export using free-drifting sediment traps also have been measured (Karl et al., 1996). These complementary measurements represent the largest data set on particle dynamics ever obtained for the NPSG.

The broad patterns that have emerged from the HOT core measurement program have many features in common with the seasonal cycles described previously for plankton dynamics in temperate and high-latitude marine ecosystems. Specifically, we have observed changes in the standing stocks of particulate matter that are consistent with a typical spring–summer bloom and fall–winter demise cycle; i.e., particulate matter increases in response to increasing solar radiation and the establishment of upper EZ density stratification, followed by EZ nutrient depletion, increased particulate-matter recycling and eventual breakdown of density stratification and

re-establishment of low particulate-matter concentrations during winter. These processes are much more subtle and sometimes even cryptic in the NPSG. Nevertheless, the long-term, time-series observations at Sta. ALOHA have now clearly revealed a coherent seasonality in particulate-matter dynamics as well as significant interannual and, perhaps, decadal scale variability in ocean processes in this region.

4.1. Depth distributions and dynamics of particulate-matter inventories

At Sta. ALOHA, the mean distributions of particulate matter within the EZ indicate the existence of a two-layered system with a transition at approximately 75 m. Above this depth, the mean concentrations of PC, PN and PP are approximately constant and below this depth there is a linear decrease in concentration with increasing water depth to approximately 200 m (Fig. 3). These depth-dependent patterns in particulate-matter concentrations are ultimately sustained by the combined processes of organic matter production, primarily through photoautotrophic processes, and organic matter removal primarily as a result of grazing and respiration losses, as well as passive (gravitational settling) and active (vertical migrations) export processes. Occasionally, open ocean PC and PN concentration versus depth profiles show secondary mid-depth maxima at sub-euphotic zone depths (400–500 m; e.g., Holm-Hansen, 1969; Gordon, 1971). Although no such features were observed at Sta. ALOHA (Table 1; Figs. 2 and 3), our sub-euphotic zone sampling interval (250, 500, 750, 1000 m) may have been too coarse to resolve them.

The original conceptual view of a two-layer system, advanced by Dugdale and Goering (1967), suggested that oligotrophic oceans would have a homogeneous, persistent mixed layer that would effectively separate the upper EZ from the lower EZ. Here planktonic assemblages would be segregated into a light-sufficient but nutrient-limited upper zone overlying a deeper light-limited but nutrient-sufficient zone. Physiological evidence for the existence of such a structure was observed by Eppley et al. (1973) in their studies of plankton dynamics in the NPSG, by McGowan and Williams (1973) with respect to plankton distributions, and by Venrick (1982) in her analyses of phytoplankton species composition. Therefore, it is not too surprising that the mean depth distributions of particulate matter also reflect these environmental zones despite the fact that these particle features have not been previously documented.

Although there have been numerous oceanographic studies in the NPSG (see summary in Karl and Lukas, 1996), only a relatively few have included measurements of particulate matter and even fewer have reported PC, PN and PP concentrations (Table 3). Methodological differences in sample collection and processing makes a strict comparison difficult; however, these independent data sets are still valuable and worthy of comparison to our measurements at Sta. ALOHA. In general, the historic particulate-matter standing stocks in the EZ compare reasonably well with the values we report herein for Sta. ALOHA (Table 3), with the possible exception of the anomalously high PC observations by Bogdanov and Shaposhnikova (1969) and the elevated PC and PN determinations of Gundersen et al. (1972).

Perhaps the most relevant study for detailed comparison is the time-series data set collected at Sta. Gollum during the 18-month period, Jan 1969–1970 (Gordon 1970, 1971). Sta. Gollum was established north of the island of Oahu at approximately 22°10′N, 158°W for the purpose of measuring PC and PN inventories and dynamics. Although the primary focus of the Gollum study was an investigation of temporal dynamics of deep water PC and PN pools, there were also

Table 3
Historical measurements of particulate carbon (PC), nitrogen (PN) and phosphorus (PP) in the euphotic zone North Pacific Subtropical Gyre. Additional summary data from the two time–series stations, Gollum and ALOHA, are presented in Table 4

Station location(s) and date	Depth interval (m)	PC (μM)	PN (μM)	PP (nM)	Mean C : N/C : P (molar)	Ref.
23.4°N, 153.4°W; Jan–May 1968	0–100	7.4–7.9	0.29–0.50	3.2–10	—	Bogdanov and Shaposhnikova (1969)
21°15′N, 158°15′W; 1969	0–100	4.53 ± 1.59	0.68 ± 0.18	—	6.7/—	Gundersen et al. (1972)
25°N, 155°W; Sept 1969	0–100	2.4–2.8	0.30–0.35	—	—	Ichikawa and Nishizawa (1975)
22°10′N, 158°W [Gollum]; Jan 1969 –June 1970	0–50	1.60 ± 0.08	0.19 ± 0.01	—	8.4/—	Gordon (1970)
15–35°N, 150°W; May 1970	surface 125 500	1.8–2.8 0.9–1.3 0.5–1.0	—	—	—	Wangersky (1975)
30–31°N, 143–147°W; Nov 1971	0–100	—	0.31 ± 0.10	—	—	Eppley et al. (1973)
28°N, 155°W; 5 cruises between 1972–1974	0–80	2.25 ± 1.29	0.17 ± 0.03	—	13.2/—	Sharp et al. (1980)
20–30°N, 155°W; 3 cruises between 1973–1974	0–135	1.8	0.19	11.0	9.5/164	Perry and Eppley (1981)
28°N, 155°W; June 1977	0–100	1.7–2.0	0.21	—	—	Williams et al. (1980)
21°25′N, 158°15′W; Sept 1982	Surface STA "C"	2.86 ± 0.57	0.41 ± 0.06	14.0 ± 1.6		Laws et al. (1984)
	Surface STA "D"	2.75 ± 0.81	0.39 ± 0.08	19.9 ± 3.7	7.0/204	
28°N, 155°W; Aug 1985	30 110	2.55 ± 0.48 1.73 ± 0.33	0.32 ± 0.06 0.26 ± 0.05	— —	8.0/— 6.7/—	Eppley et al. (1988)
8–15°N, 150°W; March 1988	0–100	2.59 ± 0.49	0.25 ± 0.05	––	10.4/—	Eppley et al. (1992)
22°45′N, 158°W [ALOHA]; Oct 1988 –Dec 1997	0–50	2.2 ± 0.03	0.32 ± 0.01	16.5 ± 4.3	6.9/133	This study

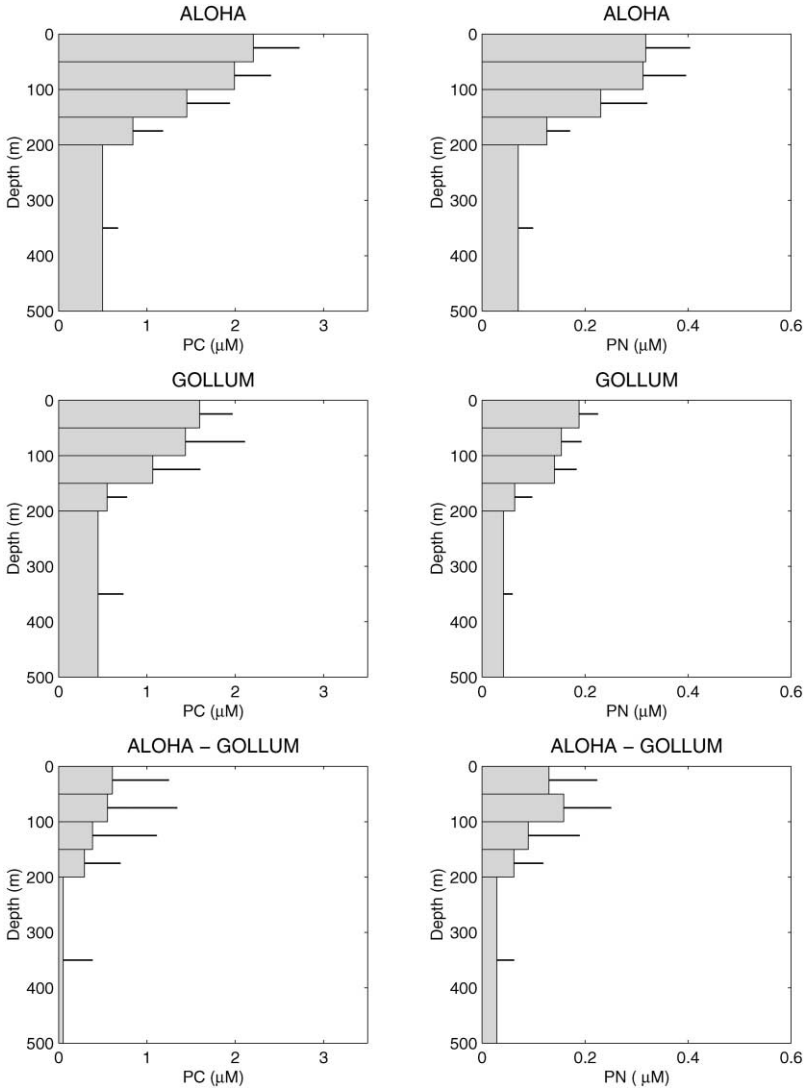


Fig. 9. Comparisons of particulate carbon (PC) and nitrogen (PN) concentrations for samples collected at Sta. Gollum (Jan 1969–Jun 1970) and Sta. ALOHA (Oct 1988–Dec 1997) as a function of depth. [Top panels]: Mean and standard deviation for PC and PN concentrations for Sta. ALOHA binned by depth. [Center panels]: Mean and standard deviation for PC and PN concentrations for Sta. Gollum binned by depth. [Lower panels]: Difference measurements (mean and standard deviation) Sta. ALOHA minus Sta. Gollum.

a reasonable number of measurements made in the upper 1000 m (Fig. 9 and Table 4). The result of this comparison indicates that EZ concentrations of PC in the more recent time period (1989–1997, Sta. ALOHA) are higher by 35–40% than PC concentrations measured two decades earlier (1969–1970, Sta. Gollum) at comparable depths (Table 4). It is equally important that the PC concentrations at depths > 200 m show no significant change indicating that the increase appears

Table 4
Comparison of particulate carbon (PC) and particulate nitrogen (PN) pool inventories for samples collected at Sta. Gollum (22°10′N, 158°W) during the period Jan 1969–June 1970 and Sta. ALOHA (22°45′N, 158°W) during the period Oct 1988–Dec 1997

Depth interval (m)	Concentrations[a]						Differences[b]		
	Sta. Gollum[c]			Sta. ALOHA			[ALOHA-Gollum]		
	PC (μM)	PN (μM)	Mean PC:PN (molar)	PC (μM)	PN (μM)	Mean PC:PN (molar)	ΔPC (μM)	ΔPN (μM)	ΔPC:ΔPN (molar)
0–50	1.597 ± 0.373 ($n = 22$)	0.188 ± 0.037 ($n = 22$)	8.5	2.195 ± 0.536 ($n = 266$)	0.324 ± 0.100 ($n = 260$)	6.8	0.598 (< 0.001)	0.136 (< 0.001)	4.4
51–100	1.437 ± 0.673 ($n = 11$)	0.154 ± 0.039 ($n = 12$)	9.3	1.964 ± 0.405 ($n = 152$)	0.317 ± 0.090 ($n = 153$)	6.2	0.527 (< 0.001)	0.163 (< 0.001)	3.2
101–150	1.067 ± 0.536 ($n = 7$)	0.141 ± 0.043 ($n = 8$)	7.6	1.461 ± 0.495 ($n = 247$)	0.234 ± 0.093 ($n = 248$)	6.2	0.394 (< 0.05)	0.093 (< 0.01)	4.2
151–200	0.549 0.227 ($n = 10$)	0.064 ± 0.034 ($n = 10$)	8.6	0.839 ± 0.364 ($n = 138$)	0.122 ± 0.045 ($n = 138$)	6.9	0.290 (< 0.05)	0.058 (< 0.001)	5
201–500	0.447 ± 0.285 ($n = 36$)	0.042 ± 0.018 ($n = 36$)	10.6	0.505 ± 0.172 ($n = 98$)	0.072 ± 0.029 ($n = 101$)	7.0	0.226 (NS)	0.030 (< 0.001)	7.5

[a] Values presented are mean values (± 1 standard deviation) for each respective depth interval; *n* represents the number of measurements that were pooled for each mean determination.
[b] Shown in parenthesis is the significance level of the [ALOHA–Gollum] difference: (NS) = not significant, others as indicated.
[c] Sta. Gollum data from Gordon (1970).

to be a manifestation of euphotic zone processes. Neither Gordon's procedures (1970, 1971) nor the one used by us for samples collected at Sta. ALOHA attempted to remove particulate inorganic carbon (PIC) prior to the PC/PN determinations. Gordon (1971) did report that PIC accounted for approximately 6% of PC (i.e., 0.09 μM C) in the upper EZ. Our PIC results for HOT-78 (Dec 1996) ranged from 0.06 to 0.09 μM C using a similar method of direct sample acidification and infrared analysis of carbon dioxide. Consequently the PC increases most likely result from changes in organic matter pools.

A similar comparison of PN concentrations in the EZ at Sta. Gollum and Sta. ALOHA reveals even larger systematic differences. Compared to the historical Sta. Gollum PN concentrations, contemporary measurements are 70–100% higher throughout the EZ; all differences are highly

significant (Table 4). The implied molar C:N ratio of the additional particulate matter (i.e., ΔPC:ΔPN) is approximately 4:1, compared to PC:PN values ranging from 6–7:1 for the bulk particulate matter. These data suggest that the standing stocks of PC and, to a much larger extent, PN in the euphotic zone have increased over the past 20–30 years.

Gordon (1977) previously summarized an important data set on the spatial and temporal variability of PC and PN in the North Atlantic Ocean, including the results of an eight cruise time-series between October 1971 and October 1973. Although subannual variations were small, there was evidence for a substantially lower PC inventory in the water column during the 1971–1973 sampling period than was measured in the same locations five years earlier. This is probably the first indication that particulate-matter inventories in the sea can vary on approximately decadal time scales. For water samples collected near Bermuda during the 1971–1973 period, Gordon reported mean 0–100 m concentrations of 14.38 μg C l^{-1} (min = 7.5, max = 38.5, $n = 25$) and 1.96 μg N l^{-1} (min = 1.0, max = 4.4, $n = 21$) for a mean C:N ratio (wt./wt.) of 7.3 (Gordon, 1977, Table 5). Similar data obtained at the Bermuda Atlantic Time-series Study (BATS) site indicate mean 0–100 m concentrations of 27.70 μg C l^{-1} ($\pm$ 9.79, min = 5.6, max = 83.8, $n = 848$) and 4.41 μg N l^{-1} ($\pm$ 1.74, min = 0.94, max = 21.21, $n = 848$) for samples collected during the period 1988–1998 (data obtained from BATS website, http://www.bbsr.edu/ctd). The mean C:N ratio (wt./wt.) for the BATS data set is 6.3. Consequently, it appears that both PC and PN in the Northwestern Sargasso Sea near Bermuda also have increased during the past two decades, again with a larger relative increase in PN, yielding a lower PC:PN ratio.

Although it is conceivable that the observed PC and PN differences that are evident in both the N. Atlantic and N. Pacific Ocean gyres stem from methodology (e.g., filter type, sample volume, instrumentation) rather than ecology, these observations are consistent with independent measurements reported elsewhere, which all suggest an intensification of N cycle processes over the past few decades. For the NPSG, Karl et al. (1995, 1997) have presented evidence that dinitrogen (N_2) fixation currently contributes a significant fraction of the annual new production at Sta. ALOHA and suggest that this may be a manifestation of changing climate conditions. The increase in particulate-matter concentrations, especially in PN standing stocks reported here, is consistent with this hypothesis and may be yet one more ecological consequence of the alleviation of N limitation during the past decade (Karl, 1999; Karl et al., 2001a, b). An enhancement of the rate of N_2 fixation over time, could have increased the supply of N resulting in a change in the carrying capacity of particulate matter both in terms of absolute concentration and relative composition (PC:PN ratio). These long-term, decadal changes in particulate-matter inventories could have profound influences on numerous biogeochemical processes in the NPSG (Karl, 1999).

4.2. Seasonal and interannual variations in particulate-matter inventories

An unique attribute of time-series data is the ability to detect low-frequency processes that may otherwise be obscured by higher-frequency processes, especially when the magnitude of the process is small relative to natural variability. By pooling data spatially (i.e., by depth) and temporally (i.e., by season and by year) we were able to detect trends that may provide insight into ecological processes and mechanisms in the surface waters of the NPSG.

The PC and PN stock assessments at Sta. ALOHA reveal a robust seasonal cycle in the upper EZ with lowest standing stocks observed in winter and highest standing stocks in summer/fall

seasons (Figs. 4, 5 and 7). Although there is also a winter season minimum in PP standing stocks, a seasonal trend is not nearly so evident (Figs. 6 and 7). The upper EZ variations in particulate-matter inventories follow the traditional boreal seasonal cycle and suggest that similar processes also may regulate open-ocean cycles, albeit in a more subtle manner. Previous investigations in the NPSG have not reported a seasonal cycle in particulate matter (Gordon, 1971; Bienfang and Szyper, 1981; Hayward et al., 1983), which may have been a consequence of temporal undersampling.

Eppley et al. (1992) reported diel PC (i.e., measured and reported as particulate organic carbon; POC) variations ranging from 3.0 to $< 2.2\,\mu M$ PC, with minima at dawn. By comparison, PN did not exhibit any diel variability. These daily variations for surface-water samples are comparable to the seasonal variations reported here. Although we do not routinely replicate the PC/PN profiles on any single cruise, 74% of all PC/PN samples during our 9-yr observation period were collected between 0600 and 1500 h (55% between 1000 and 1500 h), thus minimizing time of day sampling bias.

McGowan and Williams (1973) argued that the cycle of phytoplankton production in the NPSG was different from the classical temperate cycle. Although they did acknowledge that a single summer and winter data set may not have been adequate to describe the central-water-mass habitat, they suggested that certain physical aspects of the habitat might preclude such seasonality. As an example, they presented evidence for a well-developed pycnocline in both winter and summer, and showed winter-to-summer comparisons of phosphate and organic matter to support a suggested lack of seasonality. Likewise there was no apparent seasonality in macrozooplankton biomass, despite a significant winter increase in chl *a*.

In general, these results obtained at Sta. Climax (28°N, 155°W) are in apparent contradiction with the coherent seasonal trends reported here for Sta. ALOHA. The HOT program data set clearly reveals wintertime minima, not maxima, in particulate-matter standing stocks. It is most likely that the chl *a* trends reported by McGowan and Williams (1973) were a result of the now well-recognized seasonality in chl *a* per cell, with high values in the winter and low values in the summer caused by photoadaptation of the photoautotrophic assemblages (Letelier et al., 1993; Winn et al., 1995). These increases in chl *a* do not reflect increases in biomass (Campbell et al., 1997) or primary production (Karl et al., 1996, 1998), although it appears possible that increased winter mixing may displace some of the deep chlorophyll maximum layer (DCML) phytoplankton into the upper EZ (Letelier et al., 2000), as suggested by Venrick (1993).

Despite time-series sampling efforts including an exhaustive but short-lived 18-month study at Sta. Gollum (Gordon, 1971) and the longer duration but discontinuous Climax-region study, no seasonal cycle has been reported previously for particulate-matter dynamics in the NPSG. The reason may be that no cycle existed during these past observation periods or, more likely, that the frequency of sampling was inadequate to detect the subtle seasonal signals that do exist (Venrick, 1993). Regardless, the observed seasonality reported here for Sta. ALOHA has many features in common with the classical plankton seasonal cycle including the initiation of growth in the spring, attendant biomass increase in phase with increasing solar radiation, recharge of EZ nutrients during winter months and decrease in biomass during late fall. We suggest that the phytoplankton communities in these oligotrophic areas express many of the same seasonal growth characteristics as the temperate pattern and for essentially the same reasons.

We have previously documented pulsed nitrate additions to the upper EZ in late winter (Karl et al., 1996) and a coherent peak in ^{14}C-based primary production in summer (Karl et al., 1998) at

Sta. ALOHA. An unexpected result, however, is the observed seasonal accumulation of particulate matter during the spring and summer growing seasons, followed by a rapid loss of particulate matter from fall to winter. This is especially intriguing when one also considers that the majority of the particulate-matter pool in the EZ is comprised of non-living detrital matter (Laws et al., 1984; Winn and Karl, 1986; Karl and Dobbs, 1998), and that there appears to be a strong decoupling between rates of particulate-matter production and particulate-matter export processes (Karl et al., 1996).

The summertime accumulation of particulate matter at Sta. ALOHA may appear enigmatic as one might predict, a priori, that grazing, remineralization and other particle removal processes would all be enhanced as a result of seasonal heating of the upper EZ. However, a comparison of the observed net increase in PC from winter to summer (0–75 m depth integrated total = 37.5 mmol C) to the measured rates of primary production for the 0–75 m portion of the EZ during this period (0–75 m depth integrated total = 32.5 mmol C m^{-2} d^{-1}) reveals that the systematic accumulation of less than 1% of the primary production is all that is required for the observed seasonal PC increase. Likewise, the decrease in particulate-matter standing stocks between the maximum in fall and the minimum in winter requires only a small but sustained differential between new particle production and particle loss. Consequently, the observed seasonal dynamics in particulate-matter concentrations at Sta. ALOHA do not require any catastrophic decoupling but could result from subtle changes in any of the large number of processes that are known to affect particulate matter in the upper EZ. Among those most likely to occur at Sta. ALOHA are the temporal lag in microzooplankton and mesozooplankton standing stocks and grazing processes as primary particle production increases by nearly 50% from winter to summer (Karl et al., 1998). The subsequent decreases in particulate-matter concentrations from fall to winter would then be ascribed to the combined effects of a more intensive grazing pressure (higher micro- and mesozooplankton standing stocks) and a decreasing rate of particle production. Direct measurements of mesozooplankton standing stocks documenting summertime maxima at Sta. ALOHA (Landry et al., 2000) are consistent with this hypothesis. The coincident peaks in production and grazing in late summer could result in a peak sustained export of particulate matter during this period, a prediction that is also supported by direct observations of particulate-matter export (Karl et al., 1996).

The estimated residence time of PC (RT_{PC}) in the euphotic zone, based on measured PC inventories and PC export rates using sediment trap techniques (Karl et al., 1996) averaged 18 days (range 8–43 days), a value that is consistent with an estimate of about 15 d for a station located at 15°N, 150°W based on an independent set of assumptions (Eppley et al., 1992). Eppley et al. (1983) have also described an empirical relationship between the residence time of PC in the EZ and primary production (RT_{PC} $(d) = 25.7 \times 10^4$ [production, mg C m^{-2} d^{-1}]$^{-1.50}$). Applying this relationship to Sta. ALOHA with an average primary production of approximately 500 mg C m^{-2} d^{-1} yields a PC residence time of 23 d, which is similar to the value derived from PC inventories and export.

4.3. Particulate-matter stoichiometry

At Sta. ALOHA there are both high-frequency (seasonal) and longer-term (decadal) changes in the bulk elemental composition of the ambient particulate-matter pools (Fig. 8 and Table 2). Each year there is a systematic increase in the C : P and N : P ratios throughout the entire EZ from spring

through fall, and a decrease again in winter. These seasonal variations in the N : P ratio of the bulk particulate matter in the upper EZ with systematic increases from spring through fall are especially intriguing. The relative constancy of the PC : PN ratio suggests that the reported PN : PP variations result from changes in the PP inventories. The high PN : PP ratios in summer and fall are consistent with the proposed summertime increase in N_2 fixation and with an alternation from N plus P limitation in winter to P limitation in fall. N_2-supported new production processes lead to the accumulation of P-depleted particulate matter throughout the summer-fall periods (Karl et al., 1995, 1997).

The seasonal cycles in both the concentrations and bulk chemical composition of particulate matter suggest that the production and loss rates are decoupled on time scales of weeks to months at Sta. ALOHA. The summertime accumulation of P-depleted particulate matter (i.e., elevated C : P and elevated N : P, relative to annual average), clearly documents the hypothesized temporal decoupling of particulate-matter dynamics (Fig. 8).

Goldman et al. (1979) pointed out that the C : N : P elemental composition of phytoplankton approaches the Redfield ratio of 106C:16N:1P as cultures approach maximum growth rate. Sharp et al. (1980) reasoned that since the PC : PN ratios of bulk particulate matter in the NPSG generally exceeded the Redfield ratio (mean = 7.72, SD = 3.13), that the growth rates of phytoplankton in the gyre were probably submaximal. However, there is a caveat in this interpretation; there is no simple method to uniquely determine phytoplankton stoichiometry from that of the bulk particulate matter. By comparison, the PC : PN molar ratios of particulate matter in the upper EZ at Sta. ALOHA during all seasons were not significantly different from the Redfield ratio (Fig. 8). These results are all consistent with the hypothesis that both primary production and plankton growth rates may have increased during the past two decades (Karl and Lukas, 1996; Karl et al., 1998).

The concentration and composition of particulate matter are controlled by a complex set of production, regeneration and removal processes. In theory, an accumulation of particulate matter could result from net production of either living or non-living particulate matter, or both. Likewise, temporal variations in the stoichiometry of the particulate matter pool could reflect changes in plankton community structure and physiology, or changes in the regeneration rates or residence times of selected bioelements.

Implicit in these patterns is a decrease in the bioavailability of the ambient particulate matter either because of poor food quality, an elemental imbalance, a shift in the particle size spectrum or some other reason. While we have no direct information on these processes it is important to point out that the particulate-matter stoichiometry reported herein is based on bulk measurements of the $< 202\,\mu m$ size fraction with no attempt to characterize individual particle classes further. For example, the presence of organic matter with a bulk C : P of 150 : 1 does not preclude the presence of a subcomponent pool of P-enriched (e.g., C : P < 100) particles that may have fundamentally different dynamics. For the upper EZ at Sta. ALOHA, the bulk C : N ratio was nearly constant over the entire year whereas the C : P and N : P displayed systematic seasonal variation (Fig. 8). These results provide indirect evidence for a seasonal change in the chemical composition of the particles, despite C : N constancy. The ability to utilize particles as a food resource may be less dependent on the bulk stoichiometry than on the nature of the individual compounds that are present. Future studies need to focus on explicit chemical characterizations of the ambient pools of particulate matter.

4.4. Ecological processes at Sta. ALOHA

Because the mixed layer rarely penetrates the nutricline in the NPSG (McGowan and Hayward, 1978), it has been difficult to invoke deep winter mixing as an operative mechanism for replacement of nutrients in the upper EZ. However, stochastic and short-lived deep mixing events have been recorded at Sta. ALOHA (Karl et al., 1996; Letelier et al., 2000). These events are restricted to the late winter period and fit the pattern of bottom-up mixing that is consistent with internal-wave activity (McGowan and Hayward, 1978). Because the particulate-matter profiles presented herein represent seasonally pooled means (Figs. 7 and 8), the particulate-matter dynamics described herein may also be sustained by these episodic nutrient intrusions.

As previously discussed, the magnitude of seasonal variations in PP is relatively small compared to the PC and PN inventories, and is opposite in phase. The comparison of PP with PC and PN dynamics also reveals opposing seasonal cycles in the upper versus the lower EZ (Fig. 8). The dynamics of PP are clearly decoupled from PC and PN at Sta. ALOHA, and this also appears to be true for the dissolved matter pools as well (Karl et al., 1997, 2001a).

The emergent pattern that is revealed by these seasonally pooled data documents the temporal response of the plankton with the advance of the seasons correlating to increased light flux and, perhaps, changes in water column stratification. There is an obvious spring bloom throughout the EZ, but the largest accumulations of particulate matter are in the upper EZ where $\sim$ 70–90% of the annual increase occurs during this period. Once developed the two-layered system becomes well established with high-light-adapted species in the upper EZ and shade-adapted species in the lower EZ. Nutrient import into the EZ is most likely reduced to diffusive processes or active transport by organisms. As the seasons advance, the near Redfield ratios observed in the winter particulate-matter pools progressively deviate, perhaps in response to differential rates of C, N and P remineralization and export or to subtle changes in plankton community structure and their nutrient requirements. These systematic changes in particulate-matter pool concentrations and composition have important consequences for biogeochemical processes in these open-ocean ecosystems.

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