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Ecological nitrogen-to-phosphorus stoichiometry at station ALOHA

David M. Karl[a,*], Karin M. Björkman[a], John E. Dore[b,1], Lance Fujieki[a], Dale V. Hebel[a], Terrence Houlihan[a], Ricardo M. Letelier[c], Luis M. Tupas[a]

[a]*Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822, USA*
[b]*Aquasearch Inc., 73-4460 Queen Kaahumanu Hwy., Suite 110, Kailua-Kona, HI 96740, USA*
[c]*College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331-5503, USA*

Abstract

The elemental stoichiometry of dissolved and particulate matter in the sea, especially the nitrogen-to-phosphorus ratio, is an important parameter for studies of the nutrient control of plankton growth and for modeling biogeochemical processes, including carbon sequestration. Nitrogen (N) and phosphorus (P) pools have been measured on approximately monthly intervals for a 9-yr period at a deep-ocean station in the North Pacific subtropical gyre (Sta. ALOHA; 22°45′N, 158°W). These data sets reveal complex interactions between N and P pools, and several unexpected secular trends. Models based on steady-state assumptions will not capture these temporal variations, especially the apparently rapid response of the microbial assemblages to stochastic nutrient intrusion events and the time-varying (seasonal, interannual and decadal scale) changes in dissolved matter N : P ratios. Based on an analysis of these data, we hypothesize that the gyre is presently in a period of net fixed N sequestration and P control of plankton rate processes. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

All known organisms contain a nearly identical suite of biomolecules with common structural and metabolic functions. This biochemical uniformitarianism serves to constrain the bulk elemental composition of life. In a seminal paper, Redfield and his colleagues (Redfield et al., 1963)

* Corresponding author. Fax: +1-808-956-5059.
[1] Now at: Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI 96822, USA.
E-mail address: dkarl@soest.hawaii.edu (D.M. Karl).

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summarized much of the earlier research on C, N and P stoichiometry of dissolved and particulate matter pools in the sea and combined these data sets into an important unifying concept that has served as the basis for many subsequent field and modeling studies in oceanic biogeochemistry. The so-called "Redfield ratio" of 106C : 16N : 1P has, over the intervening decades, achieved nearly canonical status in aquatic sciences.

Despite this perceived uniformity, it is well known that the chemical composition of living organisms can vary considerably as a function of growth rate, energy (including light) availability, and ambient nutrient (including both major and trace elements) concentrations and concentration ratios (Sakshaug and Holm-Hansen, 1977; Rhee, 1978; Laws and Bannister, 1980; Tett et al., 1985). For example, under conditions of saturating light and limiting N, certain photoautotrophic organisms can store C as lipid or carbohydrate, thereby increasing their C : N and C : P ratios. Likewise, if P is present in excess of cellular demands, it can be taken up and stored as polyphosphate, causing a decrease in the bulk C : P and N : P ratios. Conversely, when the bioavailable N : P ratio is greater than what is present in "average" organic matter (i.e. $>$ 16N : 1P by atoms) selected groups of microorganisms can exhibit a metabolic "P-sparing" effect and produce biomass with C : P and N : P ratios significantly greater than the hypothesized Redfield ratios of 106 : 1 and 16 : 1, respectively. Based on theoretical biochemical arguments, Raven (1994) predicted that the C : N : P ratio in microorganisms is non-scalable with decreasing cell size. He concluded that the C : P ratio in small cyanobacteria should be higher than in average eukaryotic phytoplankton cells. Consequently, there does not appear to be a robust constraint on ecological C : N : P stoichiometry in the marine environment.

In most open-ocean habitats, there is a continuous reflux of major nutrients that over broad time and space scales is controlled by the upward eddy diffusion of dissolved inorganic nutrients balanced by the downward flux of particulate matter (Eppley and Peterson, 1979). The remineralization of sinking particulate matter within the upper mesopelagic zone of the ocean (200–500 m) sustains these large scale nutrient cycles. In the absence of other significant allochthonous nutrient sources or sinks, these coupled delivery and removal processes control both the elemental stoichiometry of dissolved and particulate pools and, ultimately, the ability of the ocean to sequester atmospheric carbon. In this regard, the remineralization length scales of C versus N and P are critical to the carbon sequestration process (Christian et al., 1997). If there is no spatial or temporal separation between C and the export production rate-limiting nutrients N and P, then there can be no net carbon sequestration.

Decoupled particulate matter C : N : P export fluxes have been observed at Sta. ALOHA (Karl et al., 1996; Christian et al., 1997) thereby providing strong evidence for the existence of an active and efficient biological C pump. Although the solubilization length scales for N and P are not significantly different (249 and 248 m, respectively), both the C : P and N : P ratios in sinking particulate matter are consistently greater than the Redfield ratio (Christian et al., 1997).

Nutrient dynamics and their role in the variability of the stoichiometry of organic matter pools are a central aspect of biogeochemical studies. Within this broad research area, ecological stoichiometry is defined as the study of the balance of energy and multiple chemical elements and their ecological interactions (Elser and Urabe, 1999). As such, it includes the subdisciplines of environmental physiology, population dynamics, community organization, ecosystem function, and global biogeochemical cycles. This paper summarizes the results of nearly a decade-long field experiment in the subtropical North Pacific Ocean. Our results document a time-variable habitat

and a C : N : P composition-variable plankton community. The implied dynamics of the upper ocean dissolved and particulate inorganic and organic N and P pools are sufficiently complex and ill-constrained that detailed mechanistic modeling of these interactions may be premature. Finally, we provide ample evidence for nonsteady-state behavior of major dissolved and particulate matter pools and present a hypothesis for seasonal, interannual and decade-scale habitat variability in bioelemental cycling processes.

2. Materials and methods

2.1. Station location, cruise chronology and sample collection

Seawater samples (0–4500 m) were collected on approximately monthly intervals from Oct. 1988 to Dec. 1997, at the Hawaii Ocean Time-series (HOT) program benchmark Sta. ALOHA (22°45′N, 158°00′W). The individual field observations from these numerous expeditions are referenced by consecutive cruise numbers: H-1, Oct. 1988 through H-88, Dec. 1997. Cruise dates and other relevant HOT program metadata are available on the World Wide Web (*http://hahana.soest.hawaii.edu*).

Discrete water samples were collected at predetermined depths in 12-l polyvinylchloride (PVC) bottles attached to an aluminum-framed rosette/CTD system (Karl and Lukas, 1996). Subsamples for nutrient determinations were collected directly, without filtration, into clean, sample-rinsed, high-density polyethylene (HDPE) bottles. The water samples were then frozen in the upright position and stored at -20°C in the dark until analyzed (Dore et al., 1996). Separate, replicate collections were used to obtain: (1) "routine" measurements of nitrate plus nitrite (N + N), soluble reactive phosphorus (SRP) and organic N and P by autoanalyzer, (2) high precision and sensitivity measurements of N + N by chemiluminescence and (3) high precision and sensitivity measurements of SRP by MAGIC. Particulate matter samples also were collected for the analysis of C, N and P (Hebel and Karl, 2001). Sinking particles were collected using a free-drifting sediment trap array that was deployed at Sta. ALOHA for a period of 60–72 h on each cruise (Karl et al., 1996).

2.2. Analytical methods

All methods used in this study are fully documented in the "HOT and COLD Field and Laboratory Protocols" manual available on the World Wide Web (*http://hahana.soest.hawaii.edu*). Briefly, automated nutrient analyses were carried out using a 4-channel continuous flow Technicon Autoanalyzer II. The methods employed follow those recommended by Technicon Industrial Systems (1973, 1979) with only slight modifications to surfactant concentrations, sampling rate and pump tube sizes. These analytical techniques are adaptations of the N + N method of Armstrong et al. (1967) and the SRP method of Murphy and Riley (1962). Distilled deionized water (DDW) was used as the diluent for all reagents and to establish the instrument baseline. Seawater refractive index and turbidity blanks were used to correct each separate analysis. Accuracy was maintained through the use of internal standards and certified reference materials (CSK; Ambe, 1978). The detection limits and analytical precision estimates for these autoanalyses were: N + N detection limit = 0.03 μM, precision = ±0.3% and SRP detection limit = 0.02 μM, precision = ±0.5%.

These stated precision estimates are for samples with N + N and SRP concentrations $> 0.2\,\mu M$ and $> 0.4\,\mu M$, respectively. Below these concentrations, we estimate the precision to be on the order of the value of the detection limit (Dore et al., 1996).

Generally, the dissolved inorganic N and P concentrations of near surface waters (< 100 m) were below the detection limits of the standard autoanalyzer procedures. For this reason, we employed two high-sensitivity methods, chemiluminescence for N + N and MAGIC for SRP. The high-sensitivity N + N method is based on the procedure described by Garside (1982) and used a commercial chemiluminescence nitrogen analyzer (Antek model 720; Dore and Karl, 1996). Accuracy was maintained by dilute CSK certified reference materials (Ambe, 1978). The precision at N + N < 50 nM averaged ± 0.5 nM, and at concentrations > 50 nM the average precision was 1.6% (Dore and Karl, 1996). Water samples from the upper euphotic zone (0–100 m) at Sta. ALOHA typically had N + N concentrations in the 1–10 nM.

The high sensitivity SRP technique used in this study was based on the MAGIC (MAGnesium Induced Co-precipitation) technique described by Karl and Tien (1992). Frozen samples were thawed in a water bath and brought to ambient laboratory temperature. Subsamples for MAGIC (typically 3 replicates, 40 ml each) were decanted into disposable 50-ml polypropylene centrifuge tubes. A high-purity NaOH solution (Fluka, 1 M) was added at a ratio of 1 : 40 (NaOH/sample; vol/vol basis) to form $Mg(OH)_2$ (Karl and Tien, 1992). The samples were capped, mixed vigorously, and then centrifuged ($1000 \times g$; 60 min) to collect the insoluble $Mg(OH)_2$ containing the adsorbed P. Following centrifugation, the supernatant was removed by vacuum aspiration and the pellet was dissolved in 9 ml of high-purity 0.1 M HCl. At this point, the triplicate samples were treated to eliminate arsenate reactivity using the method of Johnson (1971), as previously described for Sta. ALOHA samples (Karl and Tien, 1997). The reliable detection limit for MAGIC is ~ 2–3 nM with an average precision of $\pm 5\%$ for samples with SRP concentrations in the range of 10–50 nM. Above 50 nM the precision is generally ± 2–3%. SRP determinations by either autoanalysis or by MAGIC are now known to overestimate the true concentrations of orthophosphate (P*i*) at Sta. ALOHA by a variable amount (Thomson-Bulldis and Karl, 1998). For this reason we retain the designation "soluble reactive phosphorus" throughout this paper as an operational definition for the dissolved P pool that includes both P*i* and certain uncharacterized organic compounds (Karl and Yanagi, 1997).

Total dissolved N (TDN) and total dissolved P (TDP) were measured using autoanalysis following sample exposure to high-intensity ultraviolet (UV) irradiation (Armstrong et al., 1966). For TDN, the samples were exposed for a 24-h photo-oxidation period (1200 W lamp, $84 \pm 6^{\circ}C$), followed by measurements of N + N and ammonium (NH_4^+) as hydrolysis products (Walsh, 1989). For TDP, the samples were exposed to UV (1200 W lamp, $84 \pm 6^{\circ}C$) for only 2 h followed by SRP autoanalysis as above. Certain P-containing compounds (e.g., inorganic polyphosphates, ATP) are not completely hydrolyzed under these reaction conditions. However, these UV-refractory compounds are apparently not a significant portion of TDP in seawater samples collected at Sta. ALOHA (Karl and Yanagi, 1997). Independent TDP estimation using high-temperature persulfate digestion methods indicates that the two methods return similar TDP estimates when replicate Sta. ALOHA seawater samples are analyzed (Thomson-Bulldis and Karl, 1998). Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) are assumed to be equal to ([TDN] − [N + N]) and ([TDP] − [SRP]), respectively. According to this scheme, NH_4^+ that was not measured directly would be treated as a component of the DON pool and inorganic

polyphosphates that are not measured as part of the SRP pool would be treated as a component of the DOP pool. However, for surface (0–100 m) waters at Sta. ALOHA, NH_4^+ concentrations are expected to be $<0.03\,\mu M$ and inorganic polyphosphates are expected to be $<0.005\,\mu M$ compared to [TDN] = 5–8 μM and [TDP] = 0.25–0.35 μM. Consequently, these interferences should be negligible.

The water samples used for inorganic and organic nutrient analyses were not filtered prior to analysis. Consequently, the "dissolved" nutrient concentrations reported herein may be slight overestimates of the truly dissolved pools. To evaluate the potential magnitude of this error as well as to obtain independent data on potentially coupled processes, direct measurements also were made of both the suspended and sinking particulate matter pools.

Suspended particulate matter was collected from predetermined depths using the previously described CTD-rosette sampling system. Seawater was subsampled into 12-l polyethylene aspirator bottles and filtered through combusted (450°C, 3 h) Whatman glass fiber filters (GF/F, 25 mm diameter) using a pressure filtration (4–7 psi N_2 gas) system (Karl et al., 1991). For particulate phosphorus (PP) determinations, the combusted GF/F filters were rinsed with HCl prior to use (Karl et al., 1996). Sinking particulate matter was collected using a free-drifting sediment trap array with 12 replicate cylindrical polycarbonate particle interceptor traps ($0.0039\,m^2$ mouth opening) positioned at predetermined reference depths. Only data from the 150 m traps are presented herein. The sediment traps were processed as described previously (Karl et al., 1996).

Particulate C (PC) and N (PN) were measured following high-temperature combustion using a commercial elemental analyzer (Hebel and Karl, 2001). PP was measured by SRP analysis, above, following high-temperature combustion and HCl extraction (Karl et al., 1991). Based on paired sample analyses, the suspended PN and PP generally contributed $<10\%$ and $<7\%$, respectively, of the measured "TDN" and "TDP" pools in the upper 0–100 m of the water column. At greater depths, particulate matter pools were quantitatively less important.

3. Results

3.1. Dissolved inorganic N and P concentrations versus water depth

Dissolved N + N and SRP concentrations are both low in surface waters (0–100 m) and increase substantially with depth (Fig. 1). The permanent nutricline, i.e., the depth region defined by the largest concentration versus depth gradient, is located between approximately 200–600 m. The N + N and SRP concentration maxima are located near 1000 m, and at greater water depths both nutrients exhibit reduced concentrations. Unfortunately, there is no comparable time-series data set for NH_4^+ concentrations at Sta. ALOHA, and only recently has P*i* been distinguished from SRP (Thomson-Bulldis and Karl, 1998).

Concentrations of N + N and SRP in the near surface waters are near the detection limits for the "standard" continuous flow analytical methods. Many of these values would have been reported as "below detection limits" (or more precisely, statistically indistinguishable from zero), especially for N + N, much as they have been for previous investigations in the North Pacific subtropical gyre. However, with high-sensitivity methods (chemiluminescence for N + N and MAGIC for SRP) reliable nanomolar-level surface nutrient concentrations are now routinely available (Fig. 2).

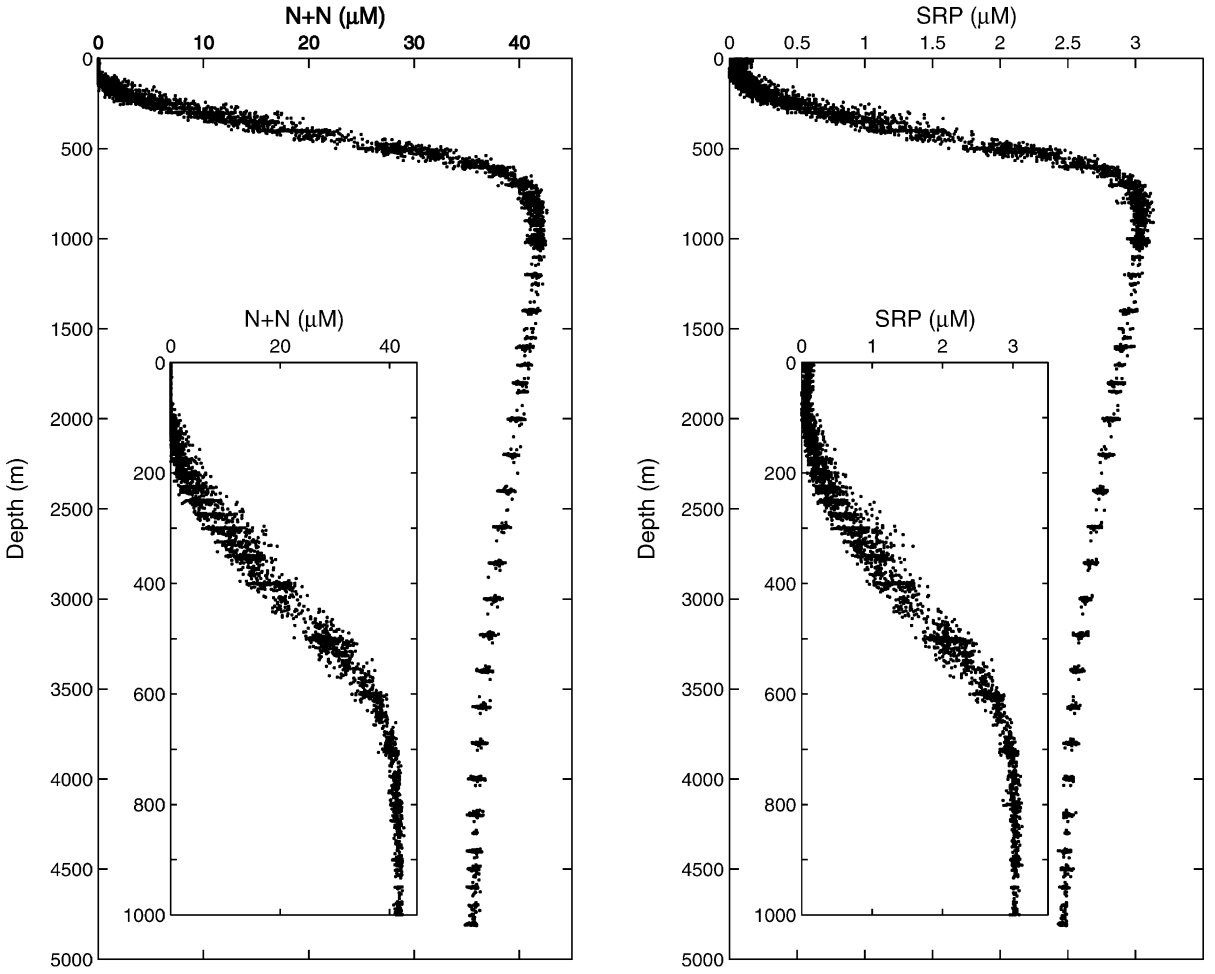


Fig. 1. Vertical distributions of nitrate plus nitrite (N + N) and soluble reactive phosphorus (SRP) for water samples collected over the entire water column at Sta. ALOHA during the period Oct. 1988 to Dec. 1997. The insets repeat those data from the upper 1000 m of the water column to emphasize the position and characteristics of the permanent nutricline where (N + N) and SRP concentrations increase dramatically with increasing water depth.

At Sta. ALOHA, the near surface N + N concentrations, though low, are both detectable and temporally variable (Figs. 2 and 3). The near-surface N + N concentrations range from <1 nM to >100 nM (Fig. 2), with generally higher and more variable concentrations and 0–100 m inventories in winter than in summer (Fig. 3). For example, the 9-yr mean 0–100 m summertime (June–Aug.) N + N inventory is 0.27 mmol N m^{-2} (s.d. = 0.26 mmol N m^{-2}) compared to a mean wintertime (Dec.–Feb.) inventory of 1.88 mmol N m^{-2} (s.d. = 3.33 mmol N m^{-2}). In addition to the generally elevated winter/spring N + N inventories, there is also a significant interannual variability with more than an order of magnitude variability in the average N + N inventory between consecutive years (e.g., compare 1993 to 1994 and 1996 to 1997; Fig. 3D).

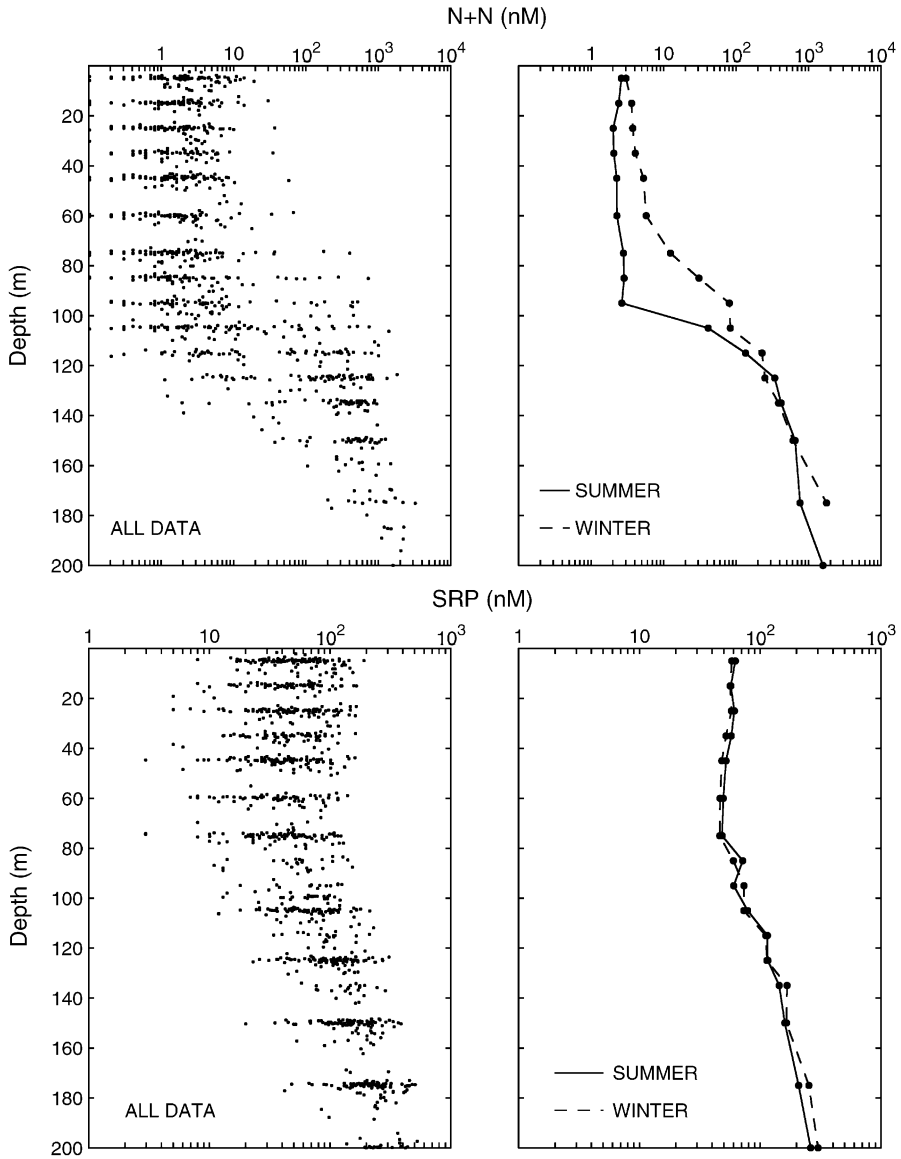


Fig. 2. Vertical distributions of nitrate plus nitrite (N + N) and soluble reactive phosphorus (SRP) for the upper 0–200 m of the water column at Sta. ALOHA, Oct. 1988 to Dec. 1997. These data sets were derived using the high sensitivity analytical procedures described in the Materials and Methods section. The data, plotted as $\log_{10}$ concentrations (nM), are presented for all seasons (ALL DATA), as well as for SUMMER (Jun.–Aug.) only and WINTER (Dec.–Feb.) only to examine seasonality. The SUMMER and WINTER data are mean values only for the full 9-yr data set.

The 0–100 m N + N inventory distribution at Sta. ALOHA reveals a highly skewed relationship of mostly low (<0.4 mmol N m^{-2}) values with occasional spikes (mean = 1.07 mmol N m^{-2} compared to a median = 0.28 mmol N m^{-2}; Fig. 3E). Given this distribution of values and the relatively high-frequency month-to-month changes in N + N inventories, it is quite possible that

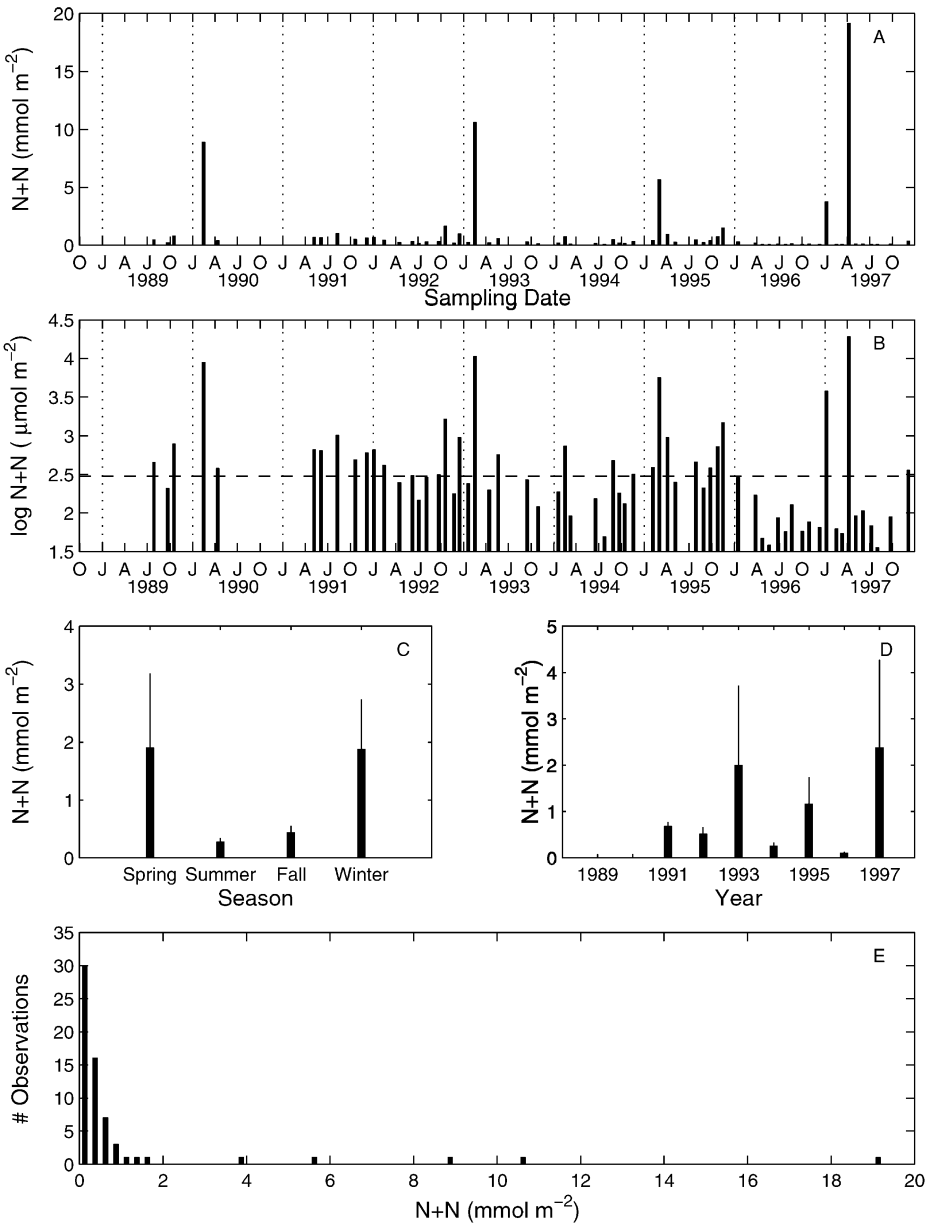


Fig. 3. Depth-integrated inventories of nitrate plus nitrite (N + N) for the upper 0–100 m portion of the water column at Sta. ALOHA during the 9-yr observation period. (A and B) Integrated (N + N) inventories versus sampling date presented as mmol m^{-2} and $\log_{10}$ µmol m^{-2}, respectively. The $\log_{10}$ presentation documents the large range in (N + N) inventories that are observed at Sta. ALOHA. The horizontal dashed line in (B) is the mean value (log µmol N m^{-2}) for the complete data set. (C) Seasonal variability in (N + N) inventories at Sta. ALOHA based on the complete 9-yr data set. Spring = Mar.–May, Summer = Jun.–Aug., Fall = Sept.–Nov., Winter = Dec.–Feb. The values presented are mean ± 1 standard deviation for each data set. (D) Interannual variability in (N + N) inventories at Sta. ALOHA. The 1989 and 1990 data sets were not included in this analysis due to an insufficient sample size ($n \leqslant 3$). The values presented are mean ± 1 standard deviation for each data set. (E) Frequency histogram of (N + N) inventories at Sta. ALOHA for the 9-yr data set. The (N + N) data were binned into 0.25 mmol m^{-2} intervals for this analysis.

the monthly sampling at Sta. ALOHA is insufficient to resolve the full spectrum of variability that might occur in the N + N pools. These periodic, pulsed N + N additions generally occur in late winter and are probably the result of mesoscale physical oceanographic processes, specifically cyclonic eddy variability and eddy-wind interactions (Letelier et al., 2000). Despite the occurrence of nutrient injections, the observed surface (0–50 m) water N + N concentrations rarely exceed 25 nM (Fig. 2).

The upper water column N + N profiles are distinguished by relatively small (or zero) concentration versus depth gradients ($\leqslant 0.1\,\mu mol\ N\,m^{-4}$) in the upper 100 m of the water column, especially in summer (Fig. 2). These near-zero gradients, also reported by Hayward (1987, 1991) for samples collected in the North Pacific subtropical gyre, would preclude any significant upward diffusional transport of N + N into the near-surface layers of the water column. However, horizontal fluxes of nutrients might still occur (Abell et al., 2000).

SRP concentrations in the upper water column at Sta. ALOHA are also near the detection limit of traditional analytical techniques throughout the year (Fig. 2). The development of the high-sensitivity MAGIC method has provided a means to obtain reliable SRP concentration estimates in oligotrophic marine ecosystems (Karl and Tien, 1992, 1997). SRP is an operationally defined pool and includes both P*i* and selected organic phosphorus compounds that hydrolyze during the procedure (Karl and Tien, 1992). SRP concentrations in the upper 0–100 m of the water column range from < 10 nM to > 100 nM, with small (or zero) concentration versus depth gradients ($\leqslant 0.05\,\mu mol\ P\,m^{-4}$) similar to the N + N depth profiles (Fig. 2).

The temporal dynamics of the near-surface SRP pools are fundamentally different from those just described for N + N pools. First, SRP concentration versus depth profiles appear to have at least three possible modes (Karl and Tien, 1997) that are not directly related to season. The mechanisms responsible for these differing patterns are still not well understood. The ambient upper water column concentrations (i.e., the 0–100 m inventory) may be as dependent on removal processes as on resupply processes, so the patterns we report here may be very much time dependent. Second, the periodic wintertime pulses that are observed for N + N are not evident in the SRP data set (Figs. 3C and 4C). Although springtime SRP concentrations are generally higher than those observed in fall, summertime concentrations exceed those measured in winter (Fig. 4C). Finally, and perhaps most importantly, the surface ocean (0–100 m) SRP inventories display a systematic interannual trend that is not observed for the N + N data set. Between 1989 and 1994, there was a continuous net removal of approximately 50% of the SRP that was present at the start of the HOT program (Fig. 4D; see also Karl and Tien, 1997). Following a brief period of SRP resupply during winter and spring of 1995, the SRP inventory decreased again to current levels that are $< 4\,mmol\,m^{-2}$, a $> 60\%$ reduction in ambient SRP for the decade (Fig. 4D). These fundamental differences between dissolved N + N and dissolved SRP strongly suggest that the dynamics of these two major nutrient pools may be decoupled at Sta. ALOHA.

3.2. Dissolved organic N and P concentrations versus water depth

DON and DOP concentrations are highest in near-surface waters (0–100 m) and decrease with increasing water depth (Fig. 5). Because these pools are calculated as difference measurements (i.e., [DON] = [TDN]–[N + N] and [DOP] = [TDP] − [SRP]), both the precision and accuracy of the DON and DOP estimates decrease with increasing depth as N + N and SRP concentrations

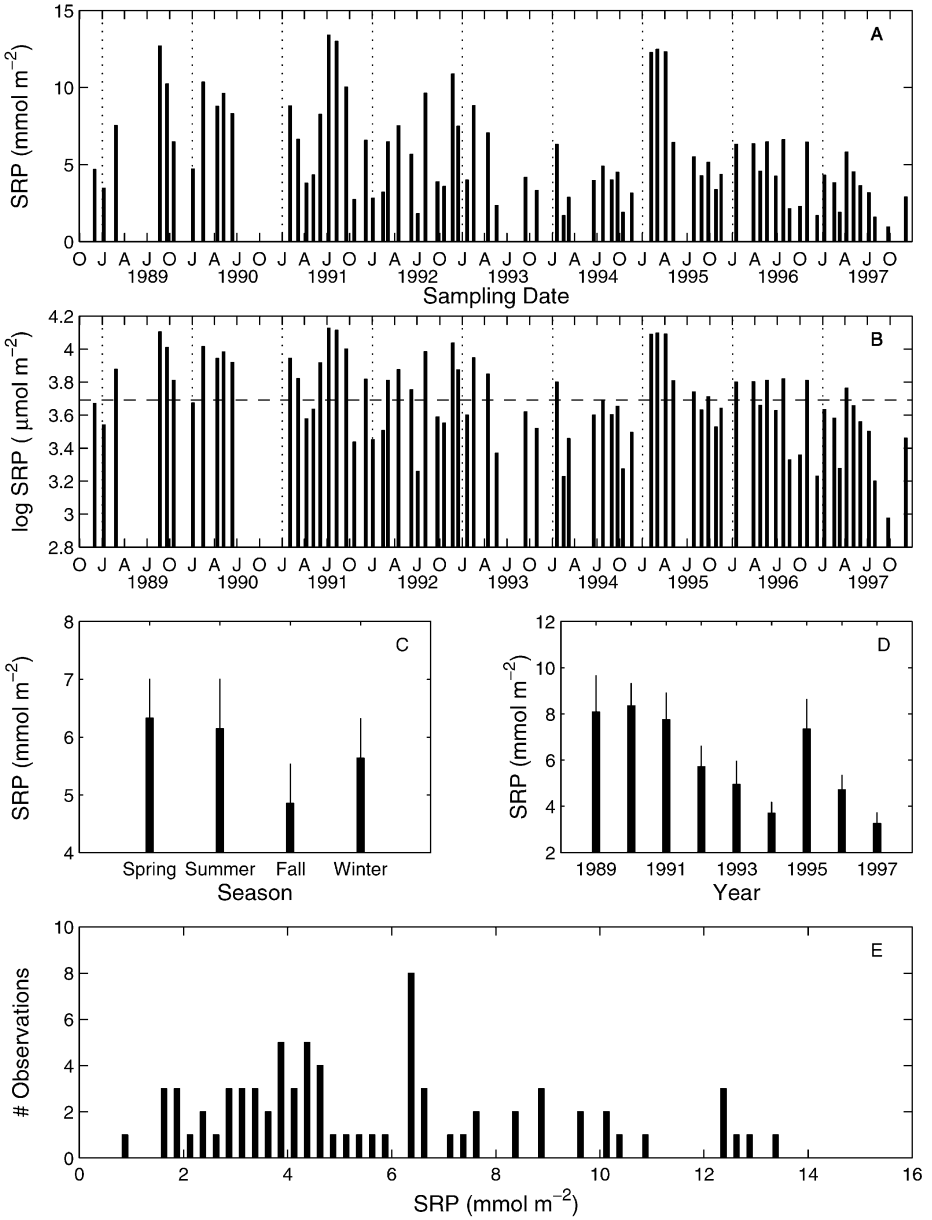


Fig. 4. Depth-integrated inventories of soluble reactive phosphorus (SRP) for the upper 0–100 m portion of the water column at Sta. ALOHA during the 9-yr observation period, as per the (N + N) data set (see Fig. 3).

become the dominant components of the total dissolved nutrient pools ($\geqslant$400 m). However in near-surface waters (0–100 m) DON and DOP dominate TDN and TDP pools, accounting for an average of $>99\%$ and $>80\%$ of the total dissolved pools, respectively (Figs. 6 and 7).

The relatively large inventories of organic nutrients at Sta. ALOHA, compared to the much smaller ambient pools of inorganic nutrients, provides a buffer against large variations in

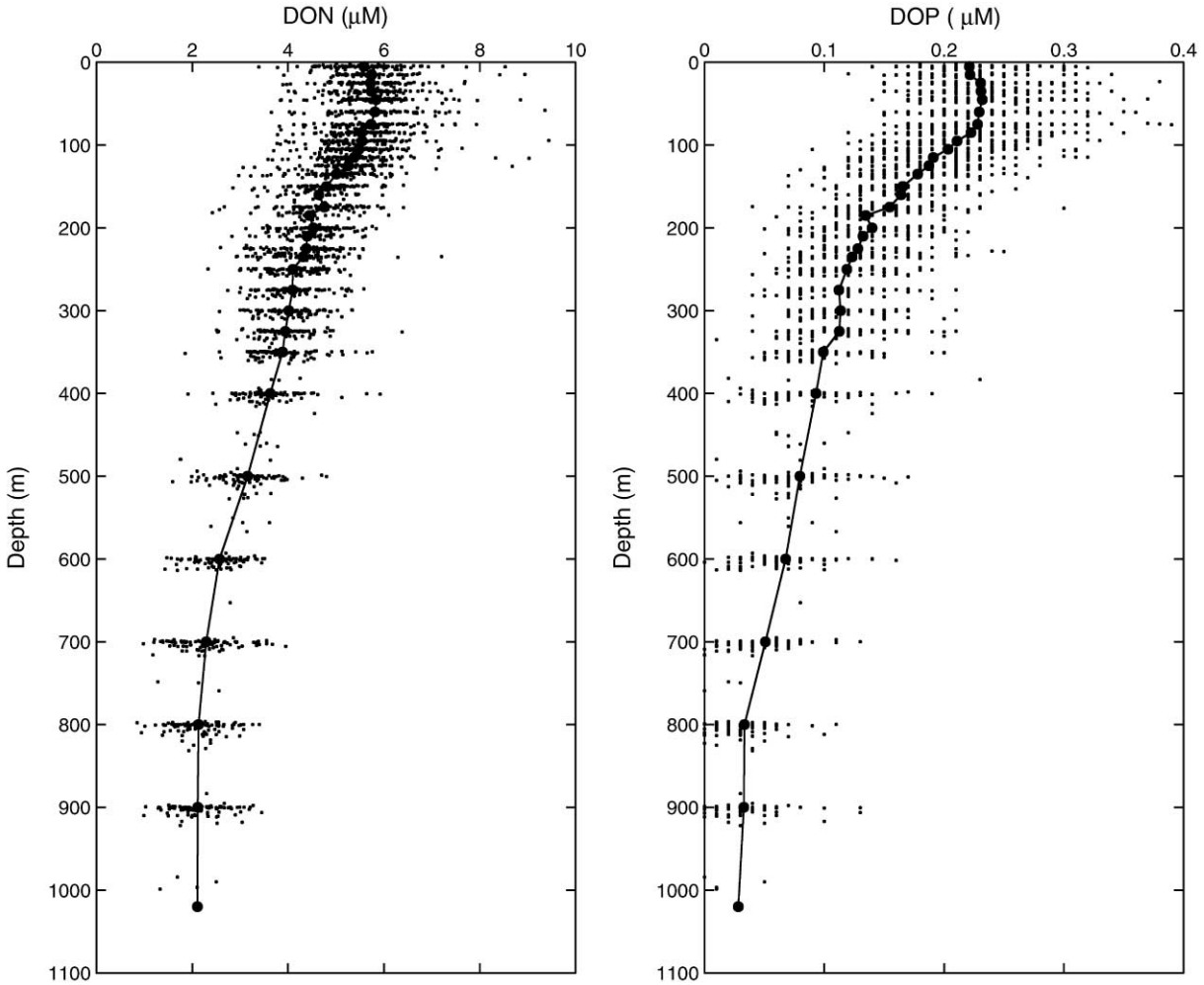


Fig. 5. Vertical distributions of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) for samples collected in the 0–1100 m portion of the water column at Sta. ALOHA during the 9-yr HOT program observation period. The large solid circles are the mean values for the full data set.

concentration with time. For example, instead of the 500-fold range observed for N + N inventories in the upper 0–100 m portion of the water column, DON inventories exhibit a less than two-fold variation over the 9-yr observation period (Fig. 6) with a mean value of 575 mmol N m^{-2} (s.d. = 59.1 mmol N m^{-2}; Fig. 6A). Furthermore, there is no evidence for large seasonal variations (Fig. 6C). Despite these relatively stable pool dynamics there does appear to be a small but somewhat erratic increase in DON during the 9-yr observation period (Fig. 6D). There was an approximately 30% variation between the annual means (i.e., 472 mmol N m^{-2} in 1990, compared to 611 mmol N m^{-2} in 1992).

Similar trends also are observed for DOP including low percent variability compared to SRP inventories and generally increasing inventories over the past decade (Fig. 7). The mean 0–100 m

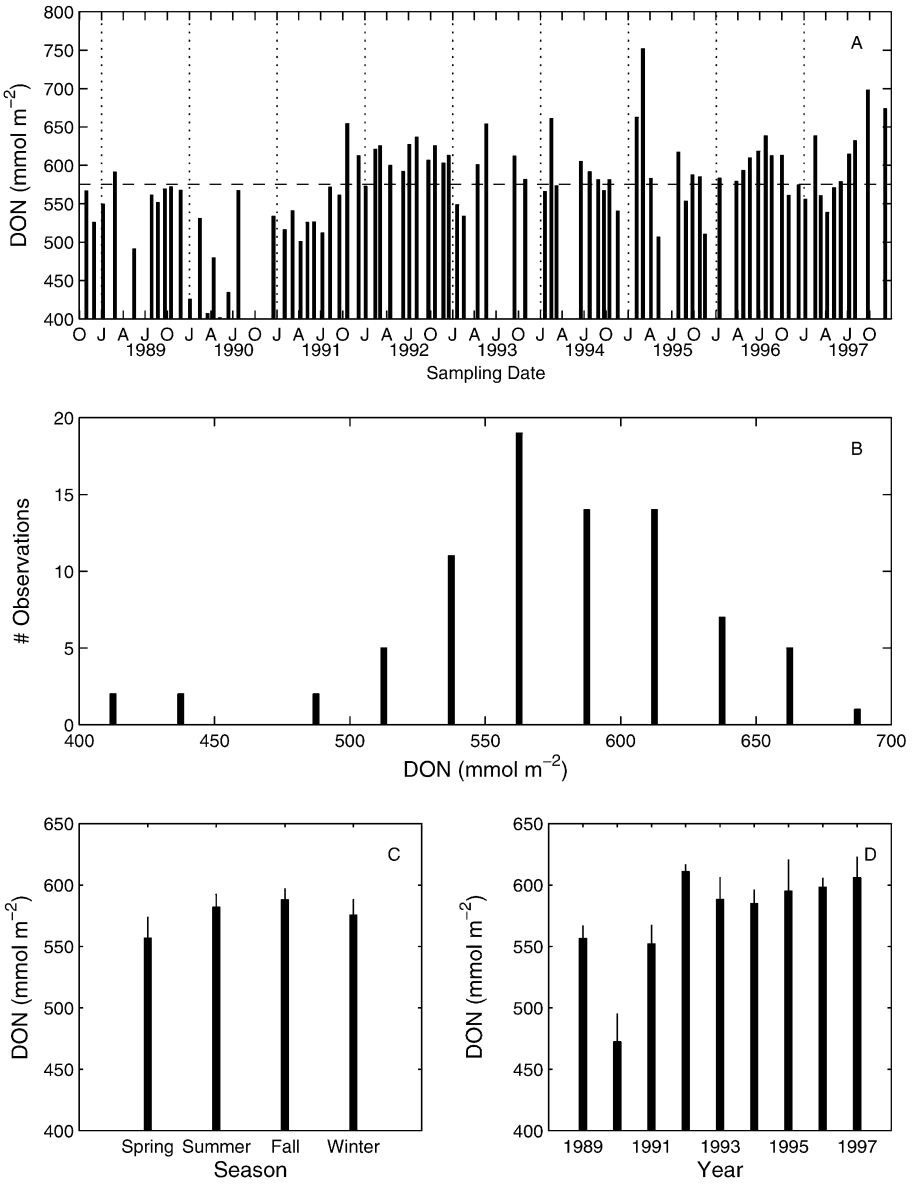


Fig. 6. Depth-integrated inventories of dissolved organic nitrogen (DON) for the upper 0–100 m portion of the water column at Sta. ALOHA during the 9-yr observation period. (A) Integrated DON inventories versus sampling date. The dashed horizontal line is the mean value for the complete data set. (B) Frequency histogram for 0–100 m depth-integrated DON inventories. (C) Seasonal variability in DON inventories at Sta. ALOHA based on the complete 9-yr data set. Seasons as defined in Fig. 3. The values presented are the mean $\pm$ 1 standard deviation for each data set. (D) Interannual variability in DON inventories at Sta. ALOHA. The values presented are mean $\pm$ 1 standard deviation for each data set.

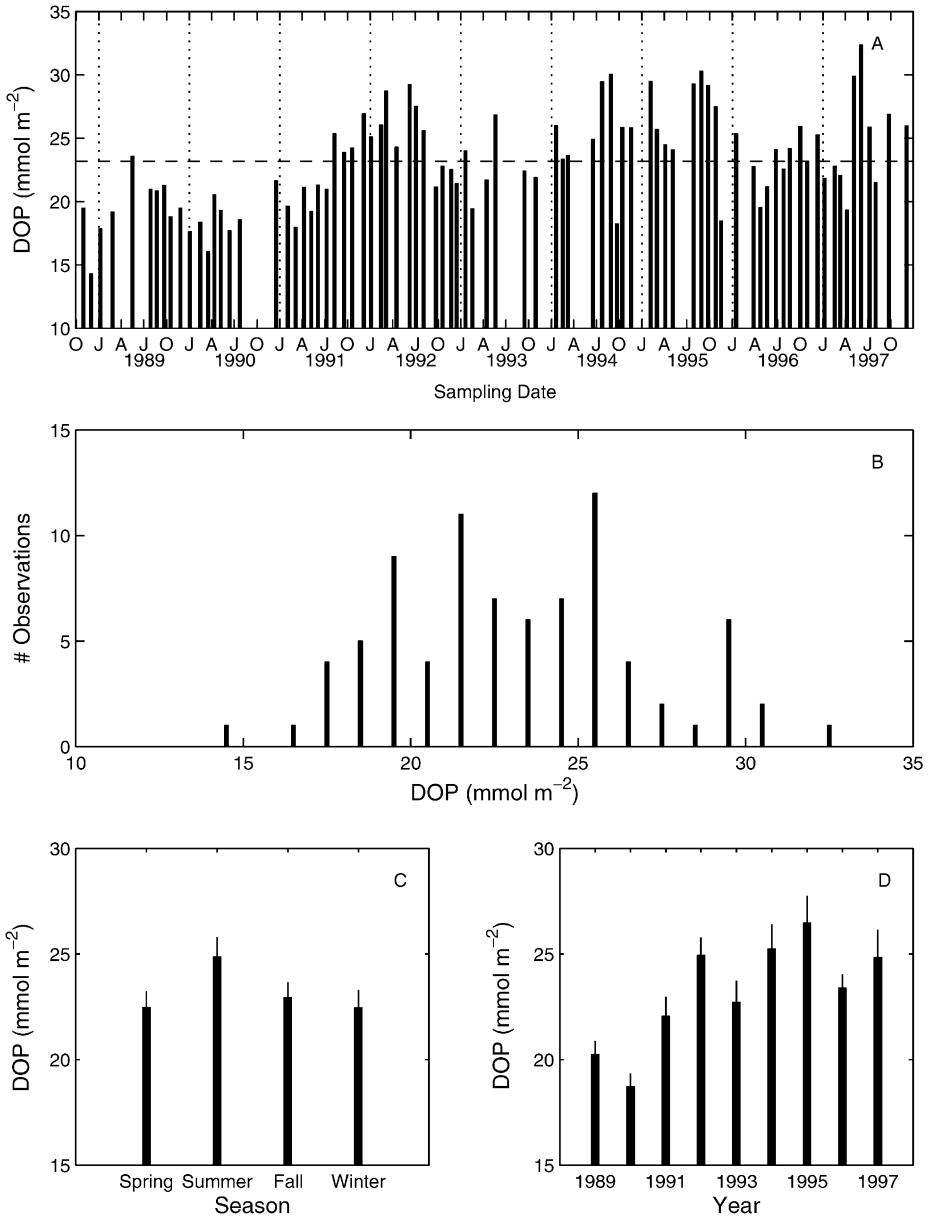


Fig. 7. Depth-integrated inventories of dissolved organic phosphorus (DOP) for the upper 0–100 m portion of the water column at Sta. ALOHA during the 9-year observation period, as per the DON data set (see Fig. 6).

depth-integrated inventory of DOP is 23.2 mmol P m^{-2} (s.d. = 3.86 mmol P m^{-2}; Fig. 7A). There was an approximately 40% variation between the lowest annual means (i.e. 18.7 mmol P m^{-2} in 1990, compared to 26.5 mmol P m^{-2} in 1995).

3.3. Dissolved matter N:P ratios

Major differences were observed for the molar N : P stoichiometries of the dissolved inorganic nutrient pools (i.e., N + N : SRP) versus the total dissolved nutrient pools (i.e., TDN : TDP) (Figs. 8 and 9). The greatest differences were observed in the upper 0–400 m of the water column (and, especially in the upper 0–100 m) where dissolved organic nutrients are present as significant fractions of the TDN and TDP pools. Whereas the dissolved inorganic N : P ratios in the upper water column were significantly lower than the Redfield ratio of 16N : 1P, the N : P stoichiometry of the total dissolved pool (inorganic plus organic) was significantly greater than the Redfield ratio by as much as 50% (Fig. 8). Furthermore, there were systematic changes in the N : P stoichiometry as

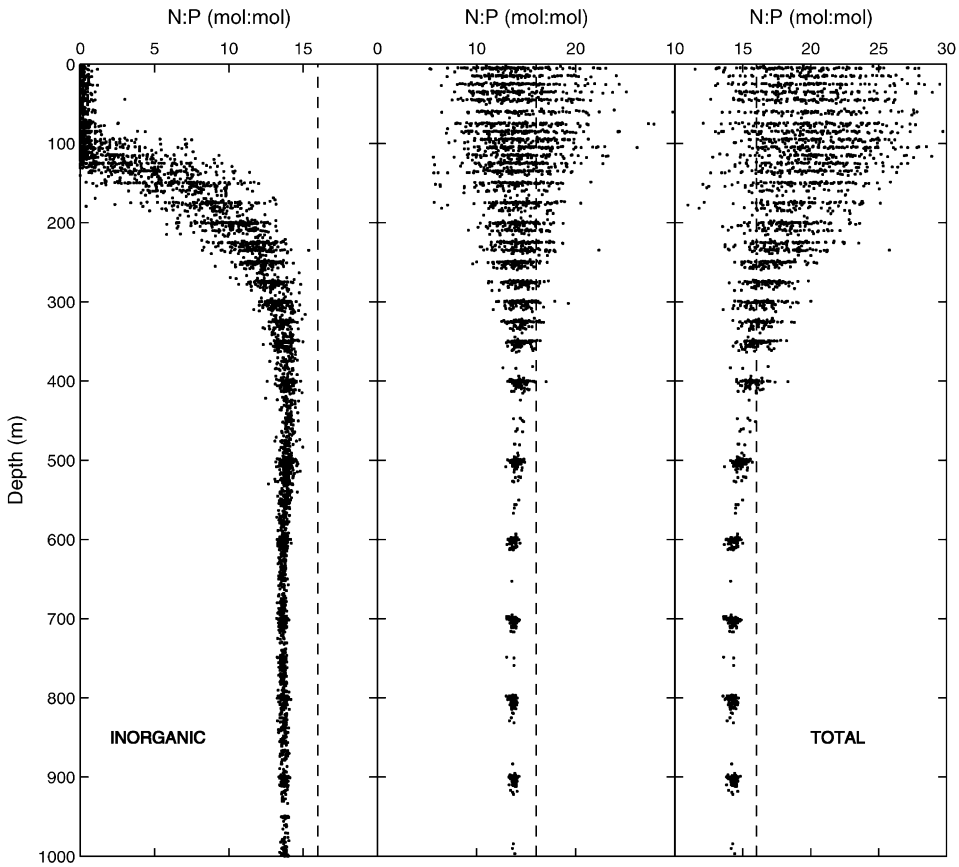


Fig. 8. Nitrogen-to-phosphorus (N : P) ratios versus water depth for samples collected at Sta. ALOHA during the period Oct. 1988 to Dec. 1997. (Left) Molar N : P ratios for dissolved inorganic pools calculated as nitrate plus nitrite (N + N) : soluble reactive phosphorus (SRP). (Center) Molar N : P ratios for the "corrected" total dissolved matter pools (see text for details). (Right) Molar N : P ratios for total dissolved matter pools, including both inorganic and organic compounds, calculated as total dissolved nitrogen (TDN) : total dissolved phosphorus (TDP). As a point for reference, the vertical dashed line in each graph is the Redfield–Ketchum–Richards molar ratio of 16N : 1P.

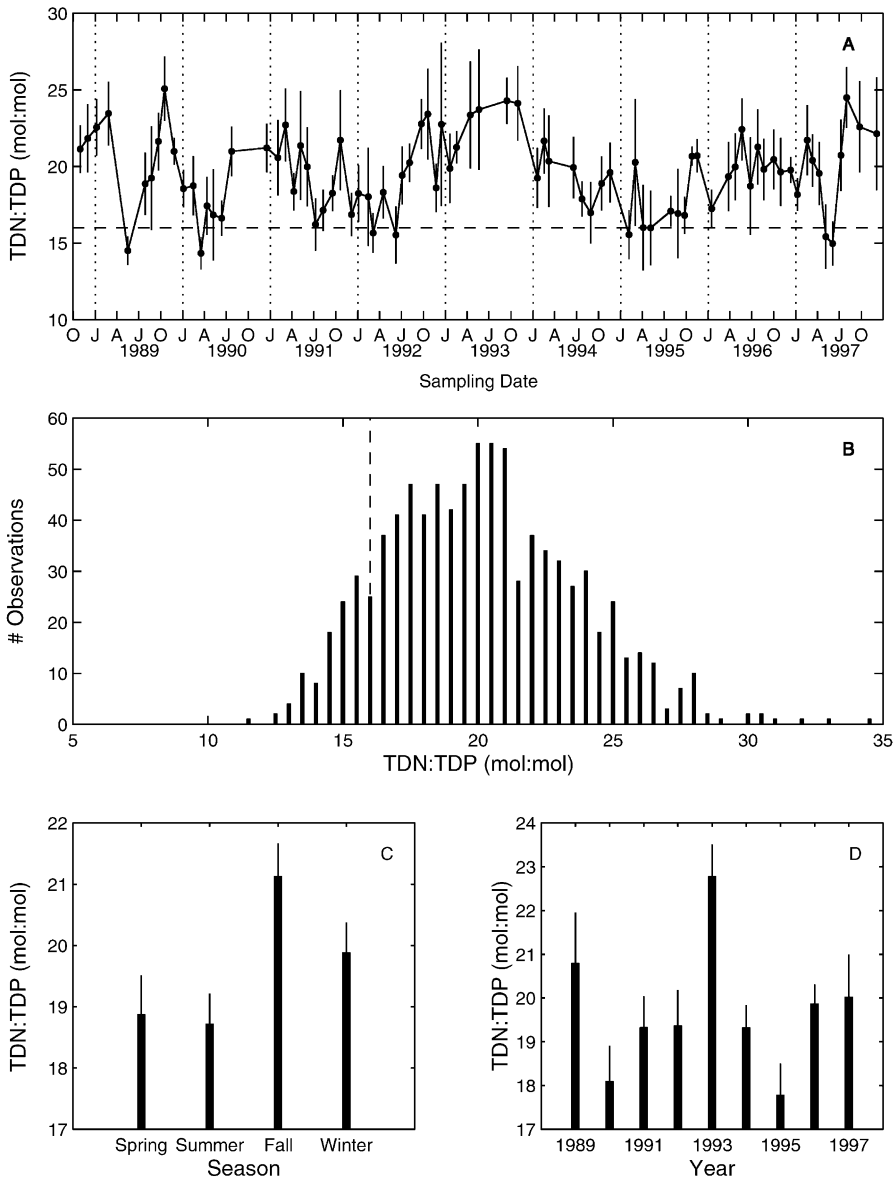


Fig. 9. Nitrogen-to-phosphorus (N : P) ratios for the total dissolved matter pools in the upper 0–100 m of the water column at Sta. ALOHA during the 9-yr observation period. (A) TDN : TDP versus sampling date. For each cruise, the mean value $\pm$ 1 standard deviation is presented. As a point for reference, the horizontal dashed line is the Redfield–Ketchum–Richards ratio of 16N : 1P. (B) Frequency histogram of TDN : TDP values for the 9-yr data set. As a point for reference, the vertical dashed line is the Redfield–Ketchum–Richards ratio of 16N : 1P. (C) Seasonal variability in TDN : TDP at Sta. ALOHA. Seasons as defined in Fig. 3. The values presented are the mean $\pm$ 1 standard deviation for each data set. (D) Interannual variability in TDN : TDP at Sta. ALOHA. The values presented are the mean $\pm$ 1 standard deviation for each data set.

a function of water depth; inorganic N : P increased towards a ratio of approximately 14, while total N : P decreased towards the same value (Fig. 8). In both data sets, the greatest rate of change in N : P with depth was in the 100–400 m region of the water column.

If TDN and TDP values are "corrected" for the mean deep water (600–1000 m) concentrations of DON and DOP (2.23 and 0.041 μM, respectively; Fig. 5), which presumably represents the more refractory pools of organic matter, the N : P molar ratio versus depth profile assumes a more normalized distribution with near-surface values distributed more or less equally around the mean deep water N : P value of approximately 14 : 1 (Fig. 8).

The stoichiometry of the TDN : TDP pools in the upper 0–100 m of the water column displayed variability on monthly, seasonal and interannual time scales. For example, our monthly observations revealed occasional high-frequency changes in the N : P ratio of the total dissolved matter pool between consecutive cruises (e.g., during spring 1989 and spring 1997; Fig. 9A). These features were characterized by decreases in the N : P ratio from values that were significantly higher than the Redfield ratio to values approximating it (Fig. 9A). When observed, these events always coincided with pulsed inputs of inorganic nutrients as detected by elevated N + N inventories (see Fig. 3). In certain years (e.g., 1991, 1993, 1996) these nutrient injections were either absent or, more likely, missed by the relatively coarse monthly frequency of our sampling program. We also observed several time periods of sustained, systematic change in the N : P ratio; e.g., Jan. 1991 to July 1992 where the N : P decreased from >20 to values equivalent to the Redfield ratio, followed by an approximately 18-month period during which the N : P ratio slowly increased back to values approaching 25N : 1P (Fig. 9A). These features resulted in significant interannual variations in the TDN : TDP ratio (Fig. 9D), with 1993 standing out as a year with an anomalously high mean TDN : TDP ratio of 22.8 (s.d. = 1.8). The mean TDN : TDP ratio for the complete 9-yr data set was 19.6 (s.d. = 2.6), well above the 16N : 1P Redfield ratio.

Regression analyses of N versus P for the dissolved inorganic and total dissolved pools document another major difference between these two data sets, namely the shift from a calculated positive "residual" P (at zero N) for the dissolved inorganic nutrient data set to a calculated positive "residual" N (at zero P) for the dissolved total nutrient data set (Fig. 10). When these data are analyzed by individual cruise, significant differences were observed in the magnitude of the calculated residual N (at zero P) for the TDN versus TDP regression analyses. There was greater than an order of magnitude variation in residual N, with concentrations ranging from a low of $<0.2\,\mu M$ to a high of $>2.5\,\mu M$ (Fig. 11). Although these variations were not well correlated with season, there does appear to be several episodes of either increasing (e.g., mid-1995 to early-1997) or decreasing (mid-1993 to mid-1995) residual N over the 9-yr observation period (Fig. 11).

3.4. Suspended and sinking particulate matter pools

Particulate N and P pools in the upper 0–100 m of the water column are small relative to the total dissolved pools (Fig. 12; also see Hebel and Karl, 2001). For PN, there is a systematic increase in summer and fall (Fig. 12) that results from an accumulation of non-living particulate matter (Hebel and Karl, 2001). This feature is not observed for PP, so the N : P ratio of suspended particulate matter increases from the winter–spring period to the summer–fall period (Fig. 12C). On average the N : P for the suspended particulate matter (mean N : P ratio = 19.4) is greater than the Redfield ratio. Despite the relative constancy of PP with season for the 9-yr data set, there is

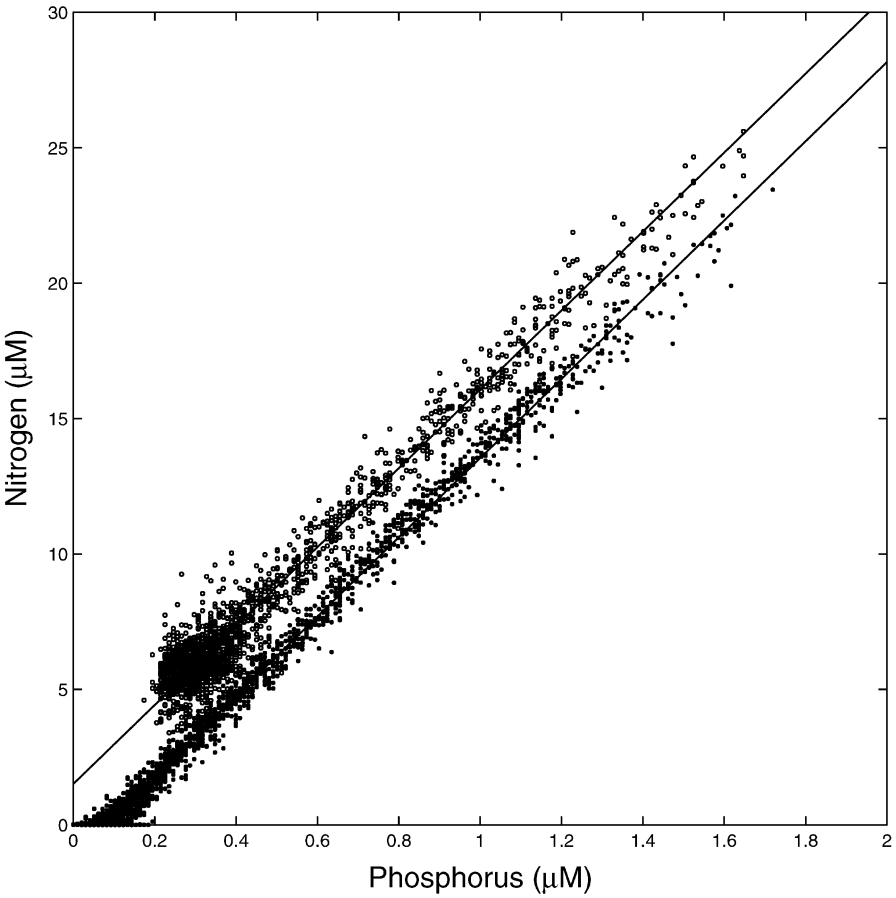


Fig. 10. Nitrogen versus phosphorus correlations for samples collected in the upper 0–400 m of the water column at Sta. ALOHA during the period Oct. 1988 to Dec. 1997. The bottom line is for nitrate plus nitrite (N + N) versus soluble reactive phosphorus (SRP) concentrations and the top line is for total dissolved nitrogen (TDN) versus total dissolved phosphorus (TDP). Model II linear regression analyses: N + N (μM) = 14.62 [14.58 to 14.66] SRP (μM) − 1.08 [− 1.10 to − 1.06], $r = 0.996$, $n = 3299$ and TDN (μM) = 14.57 [14.45 to 14.69] TDP (μM) + 1.50 [1.44 to 1.56], $r = 0.981$, $n = 2060$. Values in brackets indicate the 95% confidence intervals of the respective slope and intercept values.

a systematic, nearly 30% decrease in the 0–100 m PP inventory from a maximum in 1990 to minima in the mid-decade (Fig. 12). A more comprehensive analysis of the suspended particulate matter pools at Sta. ALOHA is presented elsewhere in this volume (Hebel and Karl, 2001).

The downward flux of PN and PP at the 150 m reference depth at Sta. ALOHA also reveals a complex temporal pattern with both high and low frequency variations (Fig. 13). On average, PN fluxes are higher in the summer period. The N : P ratio of the exported particulate matter is nearly always greater than the Redfield ratio (mean N : P ratio = 22.3), which is larger than either the mean TDN : TDP or the mean PN : PP ratios (Fig. 14). On occasion, there are short-lived "events" when the export stoichiometry of the sinking PN : PP matter appears to reset to the Redfield ratio (see Fig. 14C). This provides strong indirect evidence that the dynamics of these otherwise

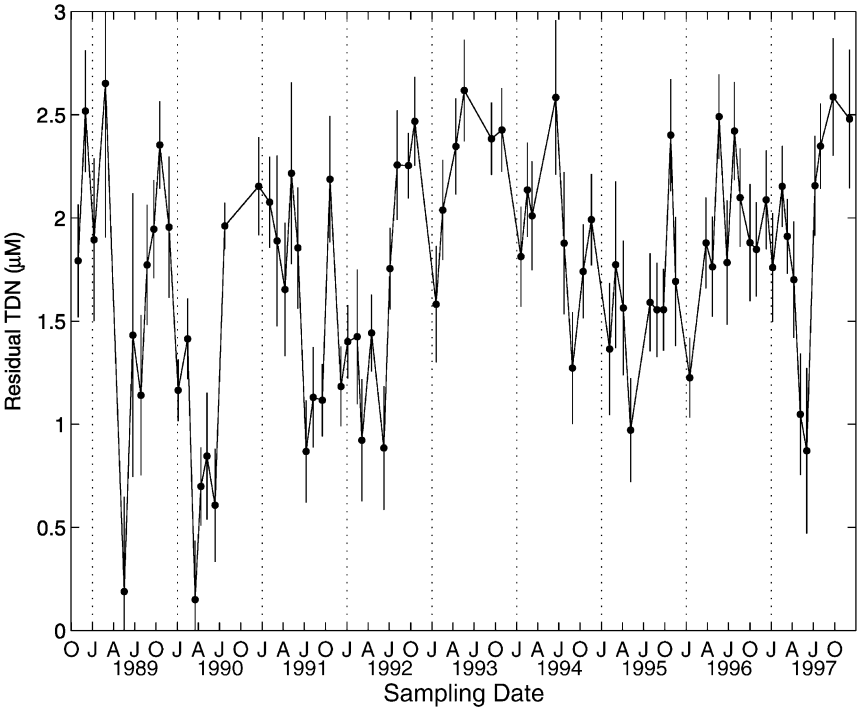


Fig. 11. Temporal variability in the estimate of residual N based on the relationship of total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) pools in the upper 0–1000 m of the water column at Sta. ALOHA, Oct. 1988 to Dec. 1997. Shown in this plot is the approximately monthly residual TDN concentration (μM), and 95% confidence interval for that value, that is calculated to exist at a hypothetical TDP = 0 μM (see text for details). These estimates are based on a model 2 linear regression analysis of TDN versus TDP (as in Fig. 10, top line) for each separate cruise. In all cases, $r \geqslant 0.997$ for these individual TDN versus TDP analyses. Residual N values ranged from 0.15–2.65 μM, with an overall mean of 1.74 μM (standard deviation = 0.57, $n = 81$).

operationally discrete pools are linked, presumably through interactions between physical and biological processes. It is also apparent that the suspended matter PN : PP ratios appear to be increasing over the 9-yr observation period (Fig. 14B), at the same time the sinking PN : PP ratios are both increasing in magnitude and degree of temporal variability (Fig. 14C).

4. Discussion

When considering nutrient limitation in the sea, including but not limited to mechanisms and consequences, it is essential to define the exact time (and space) scale of analysis. For example, seasonal or interannual patterns may differ from processes that act over longer time scales (centennial to millennial). Smith (1984) and Codispoti (1989) have reviewed the relevant literature on N versus P limitation in the marine environment. They emphasized the dichotomy between the strictly biological view and the strictly geochemical view of this issue; a reconciliation is required

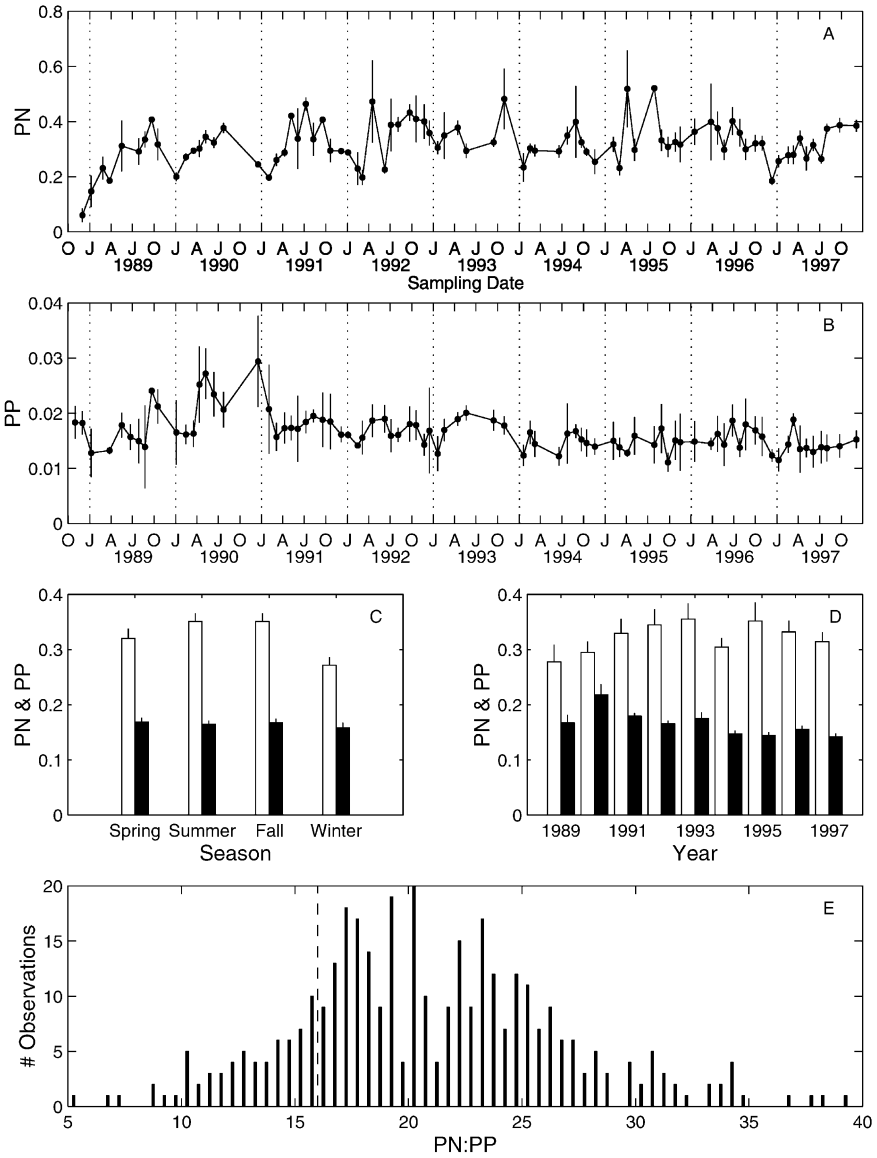


Fig. 12. Temporal variability in particulate nitrogen (PN) and particulate phosphorus (PP) pools in the upper 0–100 m of the water column at Sta. ALOHA during the period Oct. 1988–Dec. 1997. (A) PN versus sampling date. PN concentrations (μM) are mean values ± 1 standard deviation for each cruise (*n* typically 4–5 individual samples). (B) As in (A), except for PP. (C) Seasonal variability in PN and PP at Sta. ALOHA. Seasons as defined in Fig. 3. Values for PN are μM and for PP are μM × 10. Values shown are mean ± 1 standard deviation for each data set. N — unshaded bars, P — shaded bars. (D) Interannual variability in PN and PP at Sta. ALOHA. Values as in (C). (E) Frequency histogram of mean PN : PP ratios at Sta. ALOHA. As a point of reference, the vertical dashed line is the Redfield–Ketchum–Richards ratio of 16N : 1P.

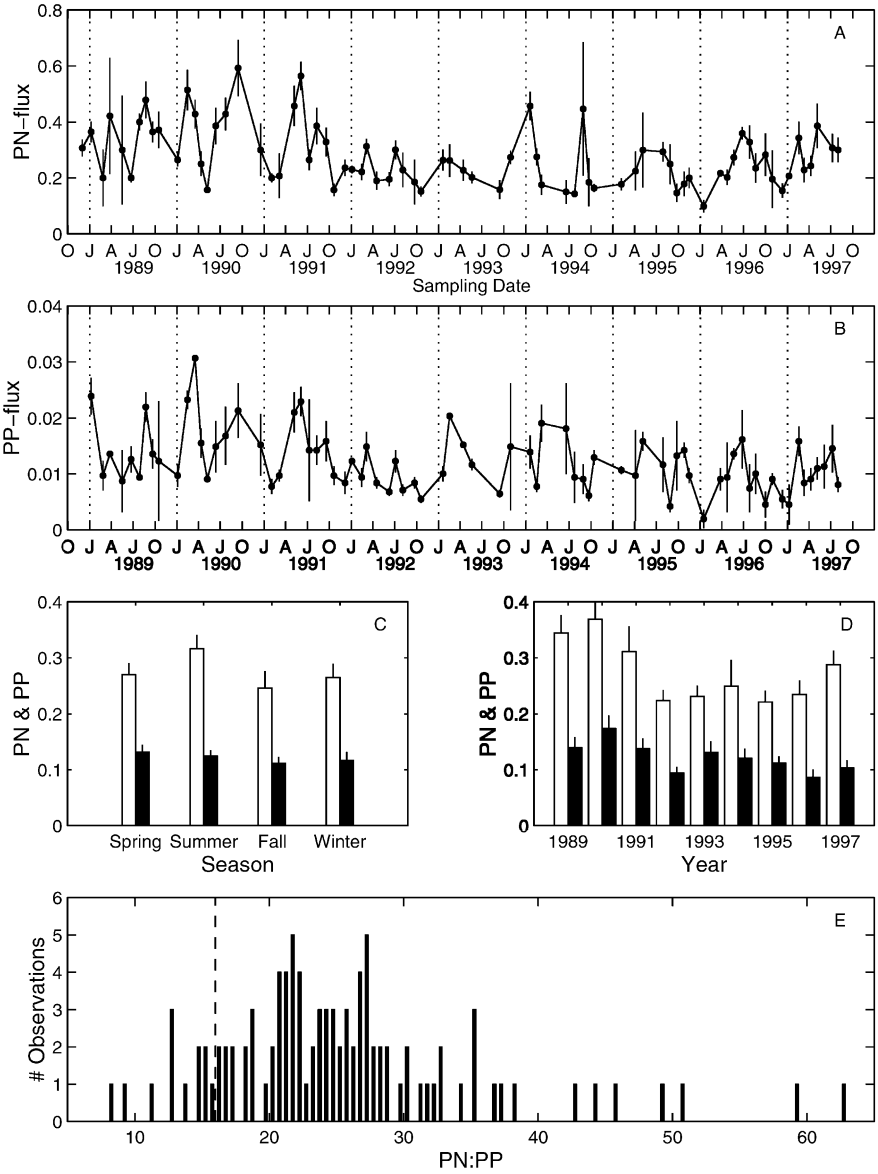


Fig. 13. Temporal variability in particulate nitrogen flux (PN-flux) and particulate phosphorus flux (PP-flux) at the 150 m reference depth at Sta. ALOHA as measured using free-drifting sediment traps. (A) PN-flux (mmol $m^{-2} d^{-1}$) versus sampling date. Each value shown is the mean $\pm$ 1 standard deviation of triplicate determinations. (B) As in (A), except for PP-flux (mmol $m^{-2} d^{-1}$). (C) Seasonal variability in PN and PP fluxes. Seasons as defined in Fig. 3. Values shown are PN flux (mmol $m^{-2} d^{-1}$) and PP-flux (mmol $m^{-2} d^{-1}$) $\times$ 10, respectively. Values shown are mean $\pm$ 1 standard deviation for each data set. N — unshaded bars, P — shaded bars. (D) Interannual variability in PN- and PP-fluxes, as in (C). (E) Frequency histogram for PN : PP ratios of sediment-trap collected materials. As a point of reference, the vertical dashed line is the Redfield–Ketchum–Richards ratio of 16N : 1P.

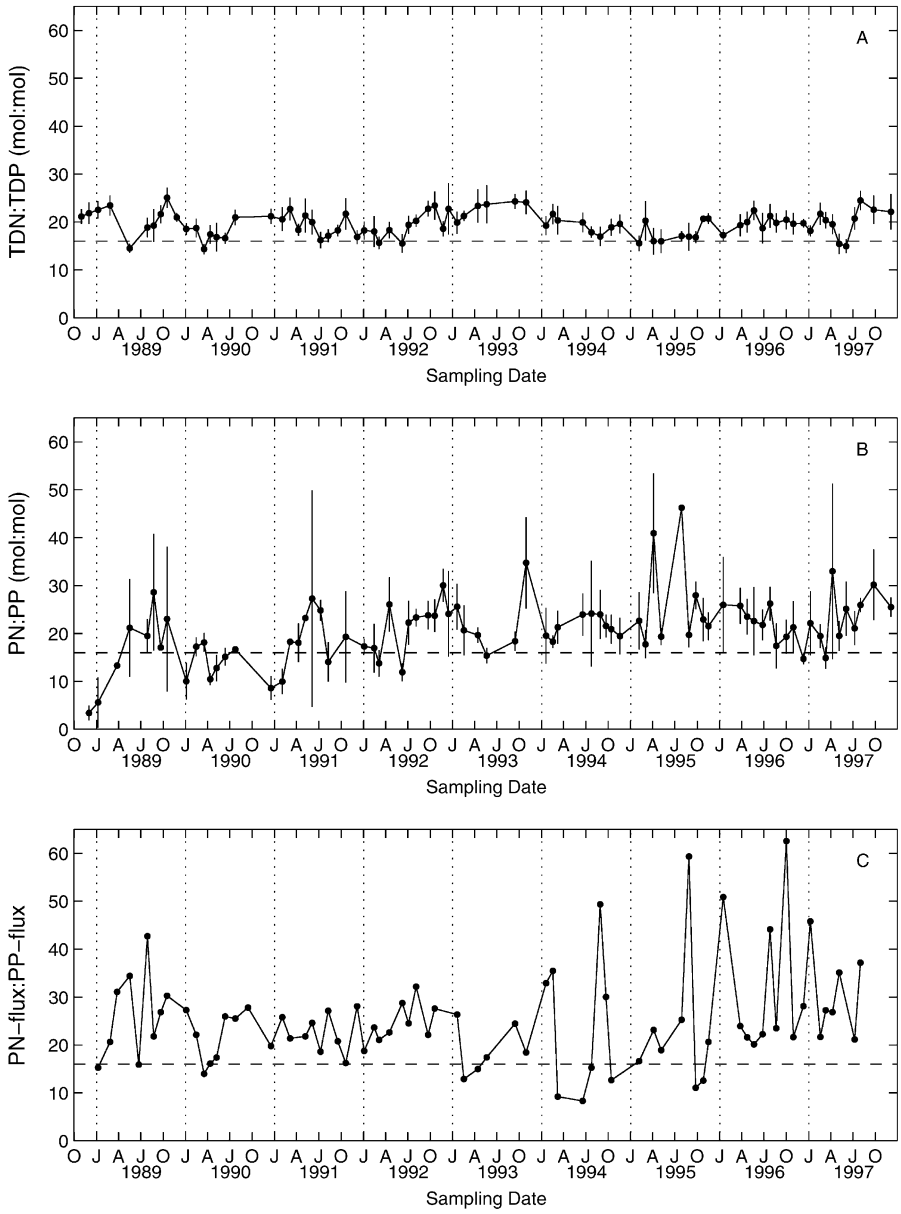


Fig. 14. Ecological N : P stoichiometry of dissolved and particulate matter pools at Sta. ALOHA. (A) N : P ratios of total dissolved matter pools in the upper 0–100 m of the water column. Each value represents the mean $\pm$ 1 standard deviation for a given cruise (n = 5–8). (B) mean N : P ratios of suspended particulate matter, as in (A). (C) Mean N : P ratios of sinking particulate matter at the 150 m reference depth. As a point of reference in each panel, the horizontal dashed line is the Redfield–Ketchum–Richards ratio of 16N : 1P.

for further progress in this important area of research (Tyrrell, 1999). In addition to time scales, spatial variability is also important as is the conceptual mismatch between the results of short-term bottle-rate measurements and ecosystem scale processes.

From the extensive 9-yr data set at Sta. ALOHA, an open-ocean subtropical habitat, it is apparent that the bulk dissolved matter N : P stoichiometry is a variable, rather than a fixed, ecosystem property. The observations reported here are in conflict with the historical view of the gyre as a monotonous, steady-state habitat. These temporal variations in the inventories and stoichiometries of both the dissolved inorganic and the dissolved organic matter pools have broad implications for the interpretation of plankton rate processes, including population adaptation and community succession, and for the ability of the oceans to absorb and sequester atmospheric carbon dioxide. However, we are still lacking an explicit model to explain fully the behavior of the dissolved nutrient pools at Sta. ALOHA including, but not limited to, the apparent decoupling of N and P pool dynamics.

4.1. Evidence for and consequences of a pulsed nutrient supply

The pathways for the resupply of bioavailable N and P in the upper euphotic zone of the North Pacific subtropical gyre are not well constrained. Potential sources include: (1) resupply from below (N and P within the permanent nutricline) by a variety of eddy-diffusion and mixing processes, (2) air–sea transport (including wet and dry deposition and, for nitrogen, gas exchange), (3) in situ production of bioavailable N via the process of microbiological N_2 fixation, (4) horizontal advection, usually along isopycnal surfaces, from regions of elevated nutrient concentrations, and (5) transport across isopycnal surfaces. The latter process could include both active (vertical migrations of plants and animals) and passive (buoyant particle flux) processes. Principal pathways for N and P export from the euphotic zone include: (1) gravitational settling of particulate matter and adsorbed dissolved matter, (2) downward diffusion and mixing, (3) active transport by plant and animal migrations, and (4) gas exchange (for N). The quantitative balance among these otherwise unrelated ecosystem processes will determine biomass carrying capacity, community structure, rates of primary and secondary production, and the ability of the ocean to absorb and ultimately sequester atmospheric carbon dioxide. If, for example, mixing of nutrients from below the euphotic zone were determined to be the most important source for new N and P, then one could estimate the net exchange of carbon and therefore the CO_2 sequestration potential.

The major source of exogenous nutrients for subtropical ocean gyres is generally thought to be the large reservoir of dissolved nutrients located in the mesopelagic zone at depths ranging from 200–1000 m (Fig. 1). Eddy diffusion and vertical mixing processes would supply N and P to the surface ocean at a ratio that is similar to that at the presumed depth of origin. From the observations at Sta. ALOHA, it is apparent that the N : P ratio varies considerably and systematically within the upper mesopelagic zone (Fig. 8). For example, if nutrients were rapidly mixed to the surface from 300 m or deeper, the N : P ratio of the allochthonous nutrients would be quite different than if the upwelled waters were derived from a depth of only 150 m. Consequently, it is imperative to understand mixing processes if a comprehensive understanding of nutrient dynamics is ever to be achieved. Unfortunately, the monthly mixed-layer depth estimation based on the static physical characteristics of the upper water column (e.g., temperature or density; see Karl and Lukas, 1996) is

insufficient to capture the stochastic events that we now believe are responsible for nutrient supply to the North Pacific gyre.

Several hypothesized mechanisms for episodic mixing have been discussed elsewhere (McGowan and Hayward, 1978; Karl et al., 1996; Letelier et al., 2000). Suffice it to say that these events are unpredictable and therefore difficult to model. The recent deployment of a physical-biogeochemical mooring near Sta. ALOHA in Jan. 1997 now provides a continuous surveillance of near-surface ocean conditions and the ability to observe high-frequency mixing events. Letelier et al. (2000) documented a strong upwelling event at Sta. ALOHA in March–April 1997 that displaced the nutricline upward by 120 m. The observed upwelling was a manifestation of the combined effects of wind-induced divergence of the surface waters and the simultaneous passage of a large cyclonic eddy through the HOT program study area. These otherwise unrelated physical processes had significant biogeochemical consequences, including a three-fold increase in chl *a* in the near surface (0–25 m), a two-fold increase in diatom abundance, and a change in the chl fluorescence efficiency. All of these changes were undoubtedly coupled to the increased supply of nutrients caused by the upwelling event.

Water samples collected on the regular monthly HOT program cruises conducted during the upwelling period (especially HOT-82, April 1997) also captured the doming upwards of the density field (Letelier et al., 2000). The large pulse of N + N observed in April 1997 (Fig. 3A) is one consequence of this enhanced nutrient supply. The other three major pulses of N + N observed at Sta. ALOHA during the 9-yr observation period all occurred in the late winter to early spring periods (1990, 1993 and 1995; Fig. 3) and are likely to have had a similar physical origin.

The response of the microbial community to these event scale phenomena will depend upon the frequency and duration of the pulse (Harris, 1980; Robarts et al., 1998). For example, short-term events have physiological consequences whereas long-duration events could lead to species shifts and ecosystem change. Consequently, the true ecological and geochemical impacts of pulsed mixing events like those reported here for the North Pacific subtropical gyre can only be assessed by comprehensive time-series investigations.

Wiegert and Penas-Lado (1995) compared the effects of upwelled pulses of nutrients to a constant supply of an equivalent annual nutrient flux. In their simulation model of an open-ocean pelagic community, nutrient pulsing produced a rich dynamical behavior and complex trophic structure that was obliterated under constant nutrient supply. These stochastic events in the subtropical North Pacific are likely to be short-lived (< 1 month) and may be undersampled by conventional ship-based observation programs. Consequently mass balances cannot be achieved without integration of a continuous measurement capability like the HOT mooring activity.

At Sta. ALOHA, the pulsed delivery of new nutrients probably occurs each winter when atmospheric forcing intensifies, density stratification weakens and cyclonic eddy activity is at its annual maximum. Yet to be explained, however, is how this deep-water entrainment per se elicits the fundamental changes in dissolved and particulate matter stoichiometry that are observed, especially the return to an approximate Redfield N : P ratio (Figs. 9 and 14). Mixing is a necessary but insufficient mechanism to explain entirely the process because of the approximately 1 month time lag observed between the presence of upwelled waters and the altered ecological stoichiometry. Clearly the microbes are largely responsible for the biochemical variations, and these changes must involve a mobilization of the very large pools of DON and DOP that dominate the mass balance and hence the average N : P ratio.

In a separate study, also conducted at Sta. ALOHA (Donachie et al., 2001), the addition of N, either as NH_4^+ or NO_3^-, to surface water samples resulted in a profound stimulation of heterotrophic microbial growth and ectoenzymatic activity. It is conceivable that the pulsed delivery of macronutrients from below is necessary to partially degrade the dissolved organic nutrients that are produced locally from a variety of microbial loop processes. This lagged pulse in organic matter remineralization purges the system of dissolved materials that have a bulk N : P stoichiometry in excess of the Redfield 16N : 1P ratio, and these are replaced with nascent dissolved and particulate matter that had been produced under nutrient-sufficient conditions with an elemental stoichiometry near the expected Redfield ratio. Regardless of the exact ecological mechanism, the pulsed delivery of nutrients appears to be an important process affecting elemental biogeochemical cycles in the euphotic zone of the oligotrophic North Pacific gyre.

4.2. N versus P pool dynamics

There are only a few historical data sets for the North Pacific subtropical gyre with which to compare the extensive 9-yr nutrient data set from Sta. ALOHA. In 1980–1981, Bienfang et al. (1984) conducted a six-cruise, time-series investigation of a coastal ocean site near Kahe Point, Oahu (21°21′N, 158°13′W). They reported that the point below which nutrient concentrations increased rapidly with increasing depth, the so-called nutrient inflection point, averaged 62 m for N + N compared to 115 m for SRP. Similar results also were obtained at a coastal ocean site off the island of Hawaii (Bienfang and Szyper, 1981). This dramatic vertical separation of N and P, if shown to be a common feature of oligotrophic regions in general, would have important implications for production and export processes.

A systematic analysis of the Sta. ALOHA data set investigating both the nutrient inflection depth (i.e., the top of the nutricline) and the nutrient slope (i.e., nutrient gradient, defined as change in concentration versus change in depth; $\mu mol\,m^{-4}$) revealed several relevant features (Figs. 15 and 16). First, while there was considerable month-to-month and interannual variability in the nutrient inflection depth for both the N + N and SRP, ranging from < 100 m to > 200 m, these temporal variations were coherent between the separate N + N and SRP data sets (Fig. 15). On average, the SRP inflection depth at Sta. ALOHA was slightly shallower than the N + N inflection depth (typically 0–10 m; Fig. 15C); the depth separation was larger when the inflection depth was shallower (Fig. 15D). Furthermore, 1993–1994 stands out as a period where this trend is reversed (i.e., SRP inflection depth $>$ N + N inflection depth). However, the mean condition at Sta. ALOHA is opposite of that observed in the 1980–1981 Bienfang et al. (1984) data set, where the inflection depth for N + N was much shallower (by 50 m) than that observed for SRP. Bienfang et al. (1984) did comment that the N versus P inflection depth separation, observed at Sta. Kahe in 1980–1981, was not characteristic of the central gyre and cited two Scripps Institution of Oceanography data reports for cruises conducted in 1968 and 1969. From this, they concluded that their interesting observations at Sta. Kahe were probably an island mass effect caused by proximity of the coastal station to the Hawaiian Ridge. This could certainly explain nutricline shoaling, but cannot easily explain the separation of the N versus P inflection depth.

"Excess" N, relative to P, could be the result of local inputs via atmospheric deposition or N_2 fixation. These N supply processes also would help to sustain the P "deficit" as the system evolved towards P limitation. Alternatively, the P deficit could have arisen from selective removal

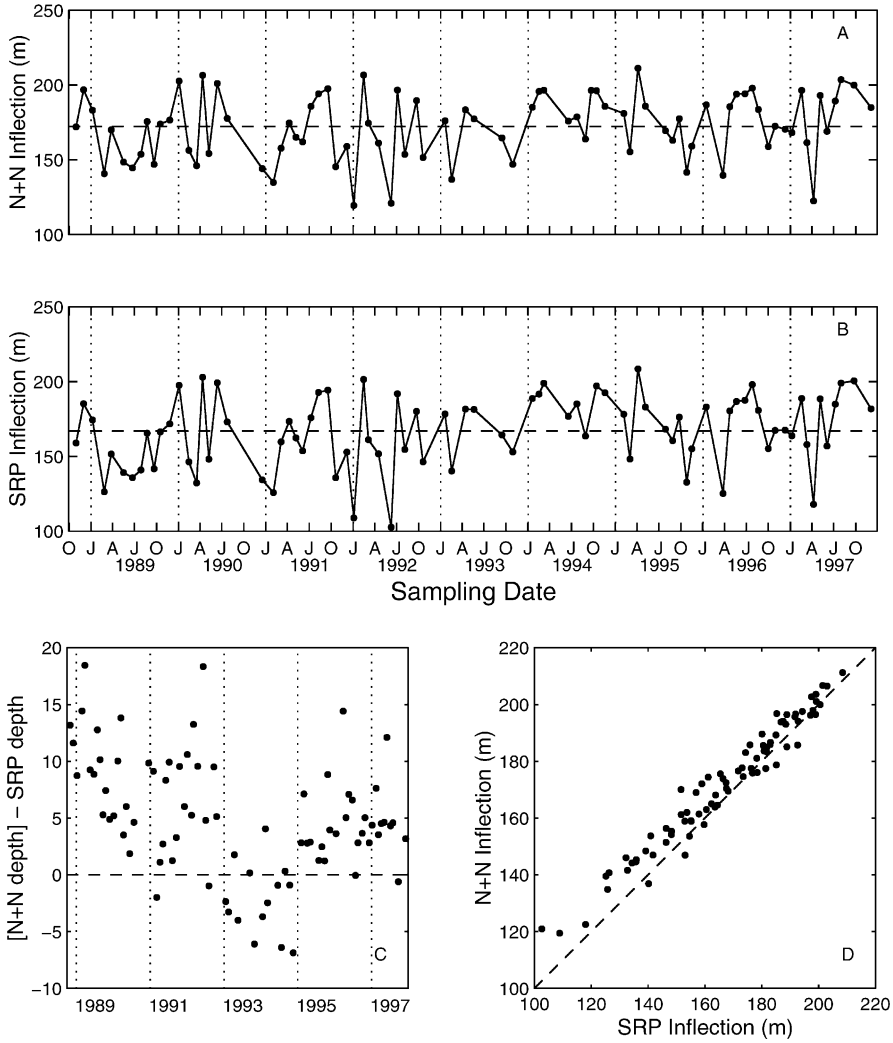


Fig. 15. Temporal variability of the nutrient inflection depth, in meters (m), for the nitrate plus nitrite (N + N) and soluble reactive phosphorus (SRP) nutricline at Sta. ALOHA (see text for details). (A) (N + N) inflection depth (m) versus time. The dashed horizontal line is the mean value for the 9-yr data set. (B) SRP inflection depth (m) as in (A). (C) Inflection depth difference plot (m) versus sampling date for the 9-yr Sta. ALOHA data set. Each point was calculated as the (N + N) inflection depth (m) minus the SRP inflection depth for each cruise. The mean of the complete data set is 5.4 m. The model 2 regression statistics are: (N + N) depth (m) = 0.90 [SRP depth (m)] + 21, $r = 0.98$. [D] Regression plot of (N + N) inflection depth (m) versus SRP inflection depth (m) for the 9-yr Sta. ALOHA data set. The dashed line is $y = x$.

processes including both biotic (vertically migrating plankton) and abiotic (adsorption) processes. Once established, the vertical separation of N and P would be maintained by the reflux of the high N + N : SRP waters. Only a very deep mixing event (significantly greater than the deeper inflection point) would reset the system back to one where N and P were supplied to the surface ocean at a ratio less than or equal to Redfield stoichiometry, as discussed above.

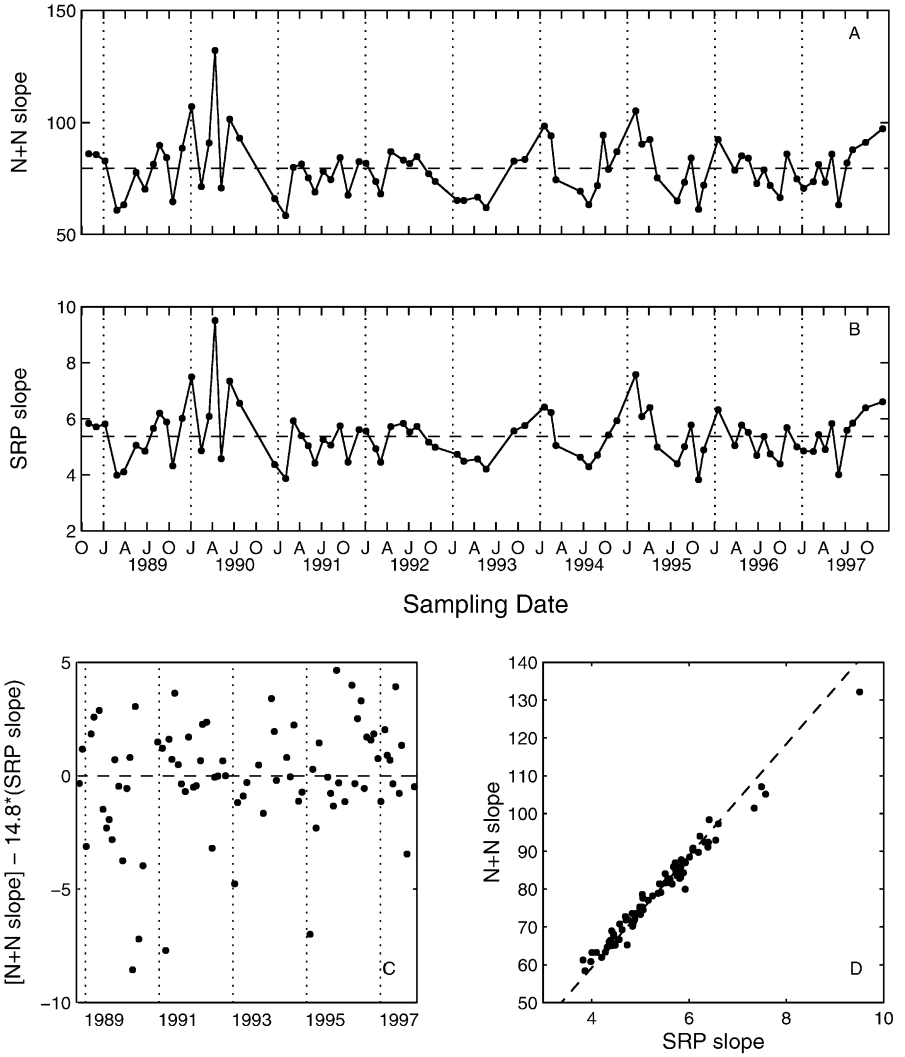


Fig. 16. Temporal variability in the slopes of the nitrate plus nitrite (N + N) and soluble reactive phosphorus (SRP) concentration versus depth relationships at Sta. ALOHA. (A) (N + N) slope (μmol N m^{-4}) versus sampling date. The dashed horizontal line is the mean of the full 9-yr data set (79.5 μmol N m^{-4}, s.d. = 12.3 μmol N m^{-4}). (B) As in (A), except for SRP (mean = 5.37 μmol P m^{-4}, s.d. = 0.93 μmol P m^{-4}). (C) Difference plot of the nutrient concentration gradients versus sampling date for the 9-yr Sta. ALOHA data set. Values shown are (N + N) slope minus SRP slope × 14.8. The constant used, 14.8, is the mean value calculated for (N + N) slope : SRP (slope) in (A) and (B). (D) Regression plot for (N + N) slope versus SRP slope. The model 2 regression statistics are: (N + N) slope (μmol N m^{-4}) = 13.15 [SRP slope (μmol P m^{-4})] + 0.0087, $r = 0.99$. Because of the non-zero intercept, the slope of this regression is different from the mean slope ratio used in (C).

With regard to the nutrient concentration gradients, there is also considerable month-to-month variability with slope variations greater than a factor of two for both the N + N and SRP data sets (Fig. 16). There is, however, a high degree of coherence in the N versus P concentration gradients (Fig. 16D). As observed for the nutrient inflection depths, the variations in the concentration

gradients are not random but appear to have episodic patterns. For example, from Dec. 1990 through Oct. 1993 the gradients were equal to or below the 9-yr mean values. By comparison, the absolute magnitude of the variation was much greater for the periods Aug. 1989 to Aug. 1990 and Aug. 1993 to Aug. 1995 (Fig. 16A and B). Nevertheless, and regardless of the magnitude of the nutrient concentration gradients in the upper mesopelagic zone, the N + N:SRP ratio was relatively constant (Fig. 16D).

The quantitative coherence between both the calculated inflection depths and the subeuphotic zone concentration gradients implies that any pulsed nutrient injections from below should deliver N + N and SRP at molar ratios of approximately 14.8 (s.d. = 0.2). By comparison to this supply ratio, the N + N:SRP of the near-surface waters (0–100 m) is consistently lower (Fig. 8), implying a net removal of N + N relative to SRP. A close examination of the 0–100 m N + N and SRP data sets reveals an unexpected pattern of these inorganic nutrient inventories, sometimes displaying elevated SRP in the absence of a corresponding N + N increase, and vice versa. For example, if one examines the five N + N peak inventories, only the April 1995 increase has a corresponding elevated inventory of SRP. Even then, the SRP inventory remains high for an approximately three-month period whereas the N + N appears to be much shorter lived. The massive increase in N + N in April 1997 showed no corresponding increase in SRP (Figs. 3 and 4).

These data imply a complex interaction between nutrient delivery, uptake, remineralization and export processes. For example, if P*i* from DOP is released more rapidly than the release of NH_4^+ from DON then there would be a temporal sequestration of N as DON and an enhancement of N_2 fixation. The fact that near surface waters have N + N:SRP ratios less than the Redfield ratio at first appears contradictory with P limitation; fluxes in addition to ambient inventories also need to be measured.

4.3. Scales of temporal variability

The observed temporal variations in the vertical position and concentration gradient of the nutricline in the upper mesopelagic zone (200–400 m) may be related to variations in the distribution of water masses, gyre circulation processes, and other ocean climate processes. For example, the nutrient slope is highly correlated with the temperature gradient in the thermocline waters, so changes in N and P slope imply changes in the vertical T gradient. Zhang and Levitus (1997) documented an advective subsurface ($\sim$250 m) thermal anomaly in the subtropical gyre that could contribute to the decadal-scale nutrient dynamics reported here. Furthermore, the intensity of the mean anticyclonic gyre circulation would directly influence the downwelling rates, and this in turn would alter the position of the nutricline and, perhaps, the nutricline concentration gradient as well. These are the fundamental parameters that establish the large-scale nutrient dynamics of the gyre and upon which the stochastic processes (e.g., cyclonic eddy- or wind-induced upwelling) are superimposed.

From available historical data, it appears that both the position and strength of these nutricline features have varied systematically over the past several decades (Fig. 17). During the early 1980s, the N + N inflection depth was significantly shallower than it is at the present time (Fig. 17A). The N and P concentration gradients also display interdecadal variability (Fig. 17C and D). Furthermore, these open-ocean data sets in the early 1980s conform to the Bienfang et al. (1984) observations documenting a $>$50 m separation between the N and P inflection depth. This

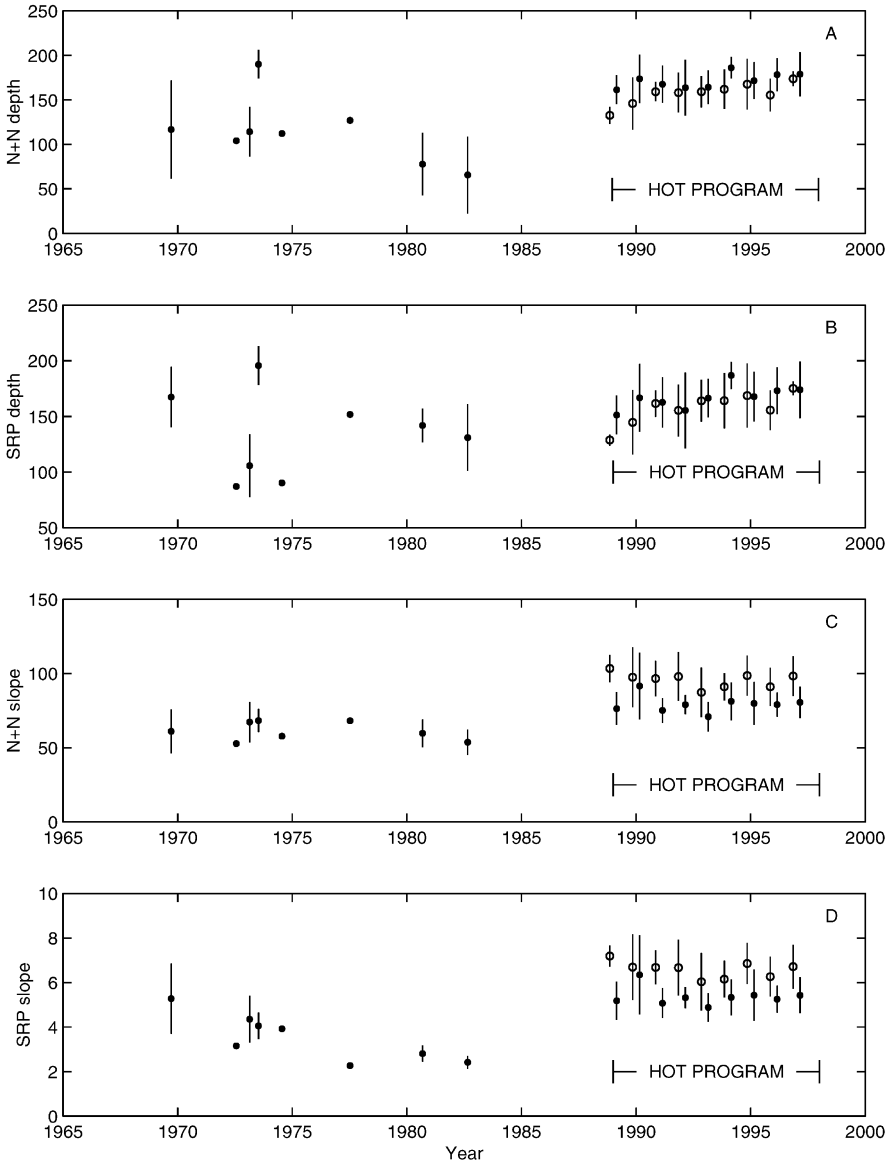


Fig. 17. Chronology of nutricline dynamics for water samples collected in the North Pacific subtropical gyre. Data shown are the mean $\pm$ 1 standard deviation for multiple profiles collected on a given cruise, or for multiple cruises in a given year (e.g., HOT program data set 1989–1997). For HOT program data, open symbols are for samples collected at the coastal Kahe Point station and solid symbols are for samples collected at Sta. ALOHA. All other data shown are from open ocean stations in the region 20–30°N, 140–170°W. Historical estimates were obtained from Climax region data reports, the GEOSECS atlas and from the World Ocean Data (WOD)-98 compilation. The 1974 data point is GEOSECS Sta. #212. (A and B) (N + N) and SRP inflection depths (m) calculated using data $\leqslant$ 400 m. (C and D) Slopes of the (N + N) and SRP concentration versus depth relationships using upper mesopelagic zone data (200–400 m).

separation feature was not evident prior to 1980 or for the HOT program data sets (Fig. 17A and B). For the HOT program data sets, there are no large differences in the contemporary N and P inflection depths measured for coastal (Sta. Kahe) versus open-ocean (Sta. ALOHA) samples collected during the period Oct. 1988 to Dec. 1997. Consequently, it is sampling date rather than proximity to the Hawaiian Ridge that controls the coherence, or lack thereof, in the N and P inflection depths.

A major and abrupt shift in the North Pacific climate system occurred during 1976–1977, manifesting itself as an intensification and eastward shift of the Aleutian low-pressure system during winter (Trenberth, 1990). These anomalous conditions persisted for at least a decade before a return to the "normal" state (i.e., the long-term climatology). For regions north of the subtropical gyre, there were a series of cold pulses corresponding to enhanced westerly winds that appeared to originate at the surface and propagated downward to approximately 400 m (Deser et al., 1996). The general surface cooling was manifest as an upward vertical extension of the 15°C isotherm in winter (Deser et al., 1996). It is conceivable that these anomalies might propagate southward with time along isopycnal surfaces and could eventually influence the nutrient balance of the subtropical gyre. The position of the 15°C isotherm in the gyre exhibits significant interannual and decadal variability with a greater than 40-m range in the mean annual depth (Polovina et al., 1994). During the period 1975–1985, the 15°C isotherm displayed a much greater depth of occurrence in the subtropical gyre than it did at the beginning of the HOT program (>250 m for the period 1975–1985, compared to approximately 230 m in 1990; Polovina et al., 1994). These gyre-scale features in the position of the main thermocline could help explain the higher rates of primary productivity that have been reported in the subtropical gyre since approximately 1982, compared to measurements made in the 1970s (Karl and Lukas, 1996).

Changes in the Aleutian low-pressure system also influence both Ekman heat transport and wind-driven ocean circulation (Yasuda and Hanawa, 1997). Estimation of the annual mean Sverdrup transport at 30°N, 130°E, where the gyre circulation is maximal, indicates an approximately 20% intensification of the rate of gyre circulation for the period 1976–1985, compared to 1966–1975 (Yasuda and Hanawa, 1997). This result is consistent with reports of similar increases in the transport of the Kuroshio Current (Qiu and Joyce, 1992). The current velocity and volume transport of the Kuroshio are coupled to the intensity of the North Equatorial Current, which in turn is influenced by the strength of the trade winds (Yamagata et al., 1985). Therefore, an intensification of the subtropical high pressure could lead to a coupled intensification of subtropical North Pacific circulation (Sawada and Handa, 1998). The upward spin of the subtropical gyre would affect the rate of general downwelling in the anticyclonic gyre and, hence, alter the inflection depth and slope of the permanent nutricline. On even longer, millennial time scales, there is evidence that the strength of the North Pacific subtropical circulation has varied significantly and has, on average, continuously weakened over the past 7000 yr (Sawada and Handa, 1998).

The Aleutian low-pressure system alternation is not an unique phenomenon and may be simply one example of a recurring pattern of interdecadal climate variability referred to as the Pacific Decadal Oscillation or PDO (Mantua et al., 1997). These large-scale atmosphere–ocean interactions can have profound effects on community structure and productivity, primarily through direct interactions with nutrient supply (Karl, 1999).

4.4. N:P stoichiometry

There remains a major misconception about the stoichiometry of dissolved and particulate matter pools in the sea. More often than not ambient pools have N:P stoichiometries that differ significantly from the Redfield ratio of 16N:1P (Duarte, 1992; Hecky et al., 1993; Elser and Hassett, 1994). While these results are oftentimes considered "unexpected", in reality they should come as no surprise. In laboratory studies, the Redfield stoichiometry is achieved only during maximum cell growth rate in nutrient-sufficient cultures (Goldman et al., 1979; Laws and Bannister, 1980). When either energy (including light energy) or nutrient limitation is imposed on prokaryotic and eukaryotic microbial populations there are systematic and therefore predictable offsets in the C:N, N:P and C:P ratios that also can affect cellular functions. The fact that particulate and dissolved matter, especially at sea, is not in "Redfield equilibrium" implies limitation, or at least control, of cell growth by exogenous energy or nutrient supplies.

Two comprehensive treatments of N:P ratios in oceanic dissolved matter have recently appeared (Fanning, 1992; Downing, 1997). In the first of these studies, Fanning (1992) used primarily the Geochemical Ocean Sections Study (GEOSECS) and Transient Tracers in the Oceans (TTO) data sets which, though of very high quality, were limited to N + N and SRP analyses. He hypothesized that if N and P had ideal Redfield model behavior (i.e., 16N:1P stoichiometry of uptake and remineralization), then a depth plot of N:P ratio of the dissolved matter pool in the oligotrophic gyres of the world ocean should produce an envelope of points for a plot of N:P versus water depth that is "T" shaped; the increased variability in the near surface waters would result from an increase in the coefficient of variation for N + N and SRP determinations as concentrations decrease to the limits of analytical detection. The most striking result of his analysis was that N:P composites from different ocean basins had different shapes. For example, the North Pacific N:P displayed a left-sided T (majority of surface data had N:P ratios less than Redfield ratio) while the North Atlantic plot was a right-sided T (majority of surface data had N:P greater than Redfield ratio). Furthermore, although the deep waters of the North Pacific Ocean (>1500 m) converged on a single N:P ratio, the value was less than the expected Redfield ratio (Fanning, 1992).

Our results for N + N:SRP at Sta. ALOHA also show the characteristic left-sided T distribution that is indicative of N limitation. We also observe a negative deep water offset from the Redfield ratio. Both features are consistent with the oligotrophic North Pacific GEOSECS data summarized by Fanning (1992). However, when one also includes the organic nutrients, DON and DOP, a fundamentally different and depth-dependent vertical distribution on the N:P ratios is observed (Fig. 8). The depth profile of TDN:TDP ratios conforms to a right-handed T distribution, again with a negative offset from the Redfield ratio. The relatively high N:P ratios in the near surface waters suggest that P, not N, is the production rate limiting nutrient in this ecosystem. This conclusion assumes that the TDN and TDP pools are fully bioavailable. However, recent research on dissolved organic matter suggests that near surface pools are comprised of at least two components: one locally produced and consumed during microbial metabolism (the labile pool), and one more refractory. Although it is impossible to quantify these subcomponents using existing analytical techniques (and in reality there may be a continuum of bioavailabilities) for the sake of the present discussion we will assume that the mean deep water (>600 m) DON and DOP pools are refractory. If TDN and TDP are corrected for these non-labile components, the depth profile of

N : P ratios assumes the characteristic T-shape (Fanning, 1992), but for a fundamentally different reason. Rather than being a consequence of analytical uncertainties at low surface ocean concentrations, as for the inorganic N : P ratio T-profiles described by Fanning (1992), we hypothesize that the T-shaped profile for the corrected TDN : TDP ratios at Sta. ALOHA is a manifestation of an alternation between periods of N limitation (left-handed portion of the T) and periods of P limitation (right-handed portion of the T). During the 9-yr observation period, conditions of P limitation were more prevalent.

In the second review, Downing (1997) convincingly documented that the euphotic zones of most open-ocean habitats have TDN : TDP greater than the Redfield ratio, indicating a deficiency of P or some element other than N. The more oligotrophic the site (as determined by total P), the higher the TDN : TDP ratio. Traditional measurements of oceanic N and P by inorganic analyses only would have led to erroneous conclusions about nutrient limitation in the North Pacific subtropical gyre. On this important point, we are in total agreement with Downing (1997).

In oligotrophic ecosystems, most of the ambient pool of dissolved nutrients is supplied by local recycling processes. For N, the recycled pools are predominantly NH_4^+ and DON. It is imperative that these regenerated N pools are included in assessments of marine nutrient dynamics and nutrient limitation. The primary limitation is the fact that DON is a heterogeneous mixture of compounds with generally unknown bioavailabilities. However, given the concentration gradients of DON in the upper 0–200 m of the water column and the near-surface concentration enrichments (Fig. 5), it seems almost certain that a majority of DON is both produced and consumed locally and is generally bioavailable, at least on time scales of weeks to months.

With regard to TDP, it is also apparent that DOP is the dominant component, although there appears to be a greater proportion of regenerated P (i.e., SRP, presumably P*i*) in the TDP pool than for N. This could be the result of a more intense recycling of P, relative to N, or to the fact that NH_4^+ (the regenerated inorganic form of N) was not measured in this study. Our inability to provide a comprehensive inventory of DON and DOP compounds (to date we have characterized $<30\%$ of the total pool) has promoted a stoichiometric assessment of the dissolved organic matter pool based on separate measurements of DOC, DON and DOP. For example, at Sta. ALOHA the "bulk" C : N : P is 333C : 23N : 1P. However, this does little to provide a biochemical characterization of the representative compound classes dissolved in seawater.

4.5. The role of N_2 fixation

Dinitrogen (N_2) fixation is one of two major microbiological processes (the other being denitrification) that can significantly influence oceanic N : P stoichiometry on global scales. This is true for both the contemporary ocean (Michaels et al., 1996; Karl et al., 1997) as well as paleoenvironments (Broecker and Henderson, 1998). Periods of enhanced N_2 fixation can decouple C–N–P cycles and affect the efficiency of the upper ocean biological carbon pump and, hence, CO_2 sequestration. Consequently, studies focused on the rates and controls of N_2 fixation are extremely relevant to both nutrient dynamics and biogeochemical processes in the sea.

Several lines of evidence from Sta. ALOHA suggest that N_2 fixation is an important contemporary source of new nitrogen for the pelagic ecosystem of the North Pacific subtropical gyre. In addition to the N : P ratios presented herein, other independent measurements and data syntheses include: (1) *Trichodesmium* population abundances and estimates of their potential rates

of biological N_2 fixation, (2) seasonal variations in the natural ^{15}N abundances of particulate matter exported to the deep sea and collected in bottom-moored sediment traps, and (3) observations of secular changes in soluble reactive P (SRP), soluble non-reactive P (SNP), and dissolved organic N (DON) pools during the period of increased rates of N_2 fixation (Karl et al., 1997). Furthermore, Zehr et al. (1998) have recently discovered the presence of potentially novel N_2-fixing microorganisms in the NPSG by amplification of previously unknown nitrogenase genes. It is conceivable, even likely, that additional major groups of N_2-fixing *Bacteria* and *Archaea* are yet to be discovered. Enhanced periods of N_2 fixation can lead to a decoupling of N and P pool dynamics and an alternation of N versus P control of primary production.

4.6. Consequences of hypothesized P limitation

Periods of enhanced N_2 fixation, as proposed for the contemporary North Pacific subtropical gyre (Karl et al., 1997), will have significant impacts on nutrient cycles. First and foremost, with an alleviation of the burden of N-control ecosystem processes evolve towards control by P (Karl et al., 1995), or essential trace metals such as iron (Wu et al., 2000). At Sta. ALOHA, the evidence for P-limitation includes: (1) the relatively high N : P ratios of dissolved and particulate matter pools (Karl et al., 1995, 1997), (2) a systematic reduction in the ambient SRP pool in the upper 0–100 m during the past decade (Karl and Tien, 1997; Fig. 19), and (3) increased microbial affinities for P*i* compared to populations investigated two decades ago (Björkman et al., 2000). These environmental conditions, in addition to the evidence presented in the previous section for enhanced N_2 fixation, are all consistent with a P-controlled habitat. Furthermore, recent evidence for the production of a high percentage of soluble to particulate organic carbon during photosynthesis (Karl et al., 1998) also may be an ecological consequence of P starvation.

Many of the features reported herein for N and P pool dynamics are also consistent with the hypothesized shift from N-to-P control of contemporary ecosystem processes. In particular, the increasing N : P ratios of suspended and particulate matter (Fig. 14) indicate a P-sparing effect on the production of organic matter in the surface ocean, a feature that is consistent with P limitation.

There are several major ecological consequences of a P-limited ocean. First is the selection for microorganisms with enhanced P*i* assimilation efficiencies. This would tend to favor small photosynthetic prokaryotes, such as *Prochlorococcus*, which presently dominate this oligotrophic habitat. Because the P*i* inventory of the upper water column decreases to less than $3\,mmol\,m^{-2}$ (Fig. 18), the average arsenate (As) : P*i* molar concentration ratio exceeds unity and should eventually affect microbial metabolism because of the well-documented competitive inhibition of As on P*i* uptake. Consequently there also would be a selection for microorganisms that are either capable of As detoxification, or those that have a high specificity P*i* transport system. Preliminary experiments conducted at Sta. ALOHA indicate that the microbial assemblages in the gyre appear to be "As-insensitive," that is to say they do not exhibit the expected As inhibition of P*i* uptake. Selection for As-tolerance also may have had other impacts on the diversity of the gyre community that have yet to be discovered.

At the present time, much of the very large and chemically diverse pool of DOP appears to be unavailable for microbial metabolism. This conclusion is based on direct measurements of the pool of biologically available P, which is generally equal to or only slightly greater than the P*i*, the preferred growth substrate. However, *Prochlorococcus* and presumably other *Bacteria* can use

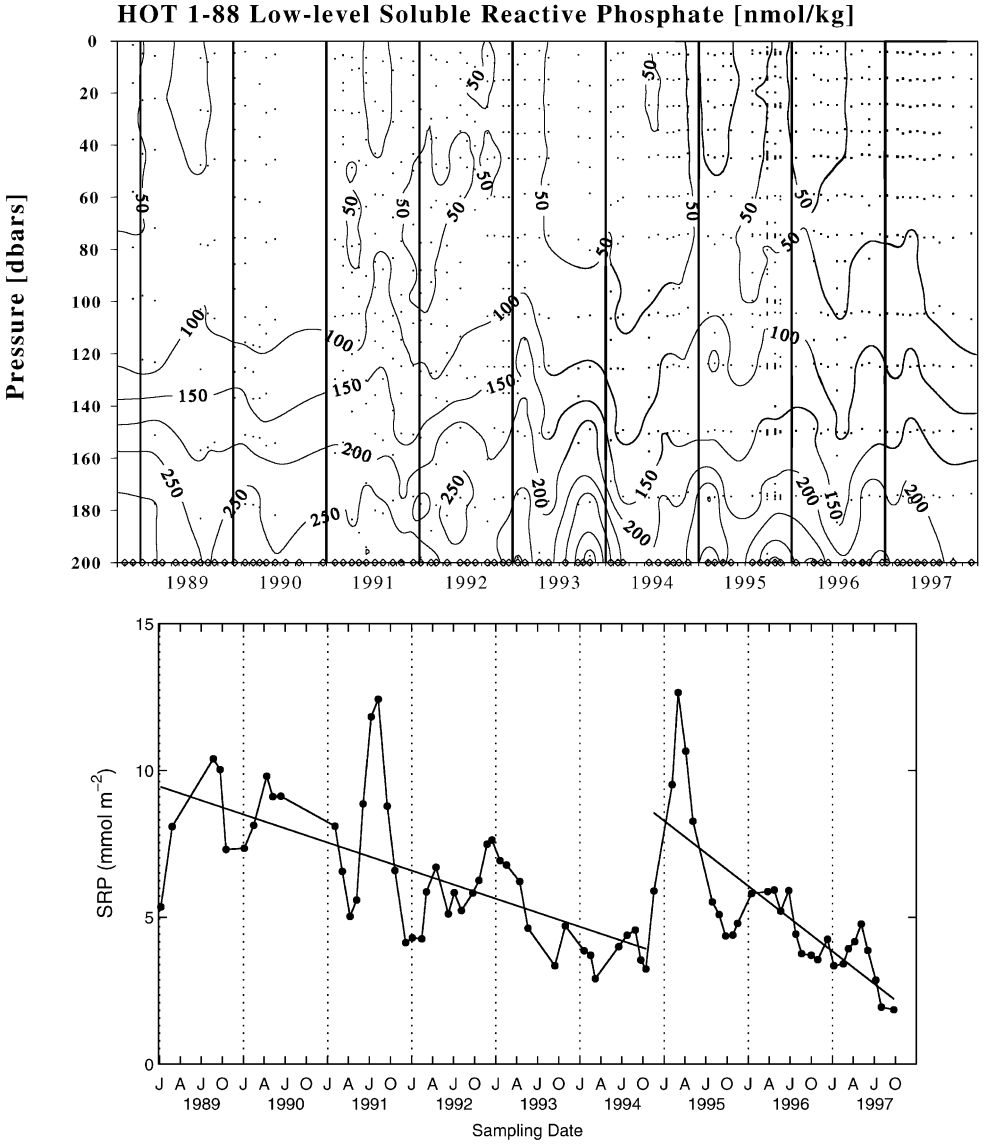


Fig. 18. Temporal variability in the SRP pools at Sta. ALOHA. (Top) Contour plot of SRP concentration (nM) versus pressure in dbar (which is approximately equal to depth, m) in the upper 200 m of the water column for the period Oct. 1988 to Dec. 1997. Contour interval = 50 nM. (Bottom) Depth-integrated (0–100 m) SRP inventory at Sta. ALOHA for the 9-yr observation period. Data shown are the 3-point running mean values for depth-integrated SRP (mmol m^{-2}). The two trend lines are the least-squares relationships for the time periods shown (1 Jan. 1989 to 31 Dec. 1994 and 1 Jan. 1995 to 31 Dec. 1997). The model I linear regression fit (bold line) for the 1989–1994 data set is: SRP (mmol m^{-2}) = 9.36 − (0.0024 × days since 1 Jan. 1989). The model I linear regression fit (bold line) for the 1995–1997 data set is: SRP (mmol m^{-2}) = 8.88 − (0.0067 × days since 1 Jan. 1995).

combined P substrates, albeit perhaps at lower efficiencies. As P*i* inventories further decrease, selection pressures for DOP utilization will increase. This could ultimately increase the availability of P and at least temporarily relieve the system of P-limitation affecting N : P stoichiometry of particulate and dissolved matter pools. This may be a partial explanation for the return to the Redfield ratio enigma observed following deep mixing. A "burst" in DOP utilization also might affect C and N cycles because the remineralization of organic phosphorus compounds is likely to mobilize other combined elements as well as P. In fact, this stimulation of DOP remineralization may already be in progress at Sta. ALOHA. The ambient concentrations of P*i*, typically $\geqslant 20$ nM, appear to be high relative to other aquatic ecosystems that are believed to be controlled by P*i* availability, which typically maintain P*i* at only a few nM or less (Cavender-Bares et al., 2001; Wu et al., 2000). Our measured P*i* uptake rates of 2–6 nM d^{-1} (Björkman et al., 2000) suggest P*i* pool turnover times of a few days at Sta. ALOHA. If periods of net remineralization of DOP and P*i* accumulation are followed by periods of net P*i* uptake, then the P*i* inventory could exhibit an oscillatory behavior even in the absence of any external physical forces. This could help to explain the enigmatic dynamics of SRP pools at Sta. ALOHA that have been presented elsewhere (Karl and Tien, 1997).

P-limitation also can have dramatic consequences for top–down control of microbial populations. The P-sparing effect exhibited by many N_2-fixing *Bacteria* yields a food resource that is also P-limited relative to the metabolic needs of the grazer populations. Elemental imbalances between producers and consumers can affect both the consumer individuals and the ecosystem (Elser and Hassett, 1994). Metazoan zooplankton regulate body quotas of N and P at fixed ratios (Sterner, 1993); therefore, when consuming food with an anomalously high N : P, P will be preferentially retained (Elser and Hassett, 1994). This mechanism could serve to decouple N and P cycles in the gyre where most of the production is supported by recycled nutrients, and could further exacerbate the P limitation of the ecosystem.

Finally, it has recently been shown that P limitation may control the frequency and pattern of viral infection for *Synechococcus* in laboratory experiments. Under conditions of P limitation, cyanophages established a non-lethal lysogenic association with the host cells (Wilson et al., 1996). Fewer than 10% of virus-infected cells lysed in P-depleted cultures compared to 100% in P-replete cultures. This results from a high viral P demand for nucleic acid synthesis in the lytic cycle. Furthermore, Bratbak et al. (1993) demonstrated in mesocosm experiments that P limitation prevented viral lysis of *Emiliania huxleyi*, whereas N limitation had no effect. If viral lysis is a major pathway for the control of microbial assemblages, P limitation may provide a temporary escape from predation, and a further sequestration of bioavailable P in living biomass.

4.7. Summary and prospectus

To date, the ocean time-series observations at both Sta. ALOHA and at our sister station in the North Atlantic subtropical gyre have provided numerous surprises, ecological insights, and unprecedented research opportunities (Michaels et al., 1999). Most of the important conclusions reported herein for nutrient dynamics and N : P stoichiometries of dissolved and particulate matter pools in the North Pacific subtropical gyre would not have been possible without the temporally resolved HOT program data sets. No single expedition, no matter how well planned, could have detected the broad spectrum of variability in key ecosystem parameters that were not anticipated

for the "stable" gyre habitat at the beginning of our research program. Although ocean time-series research is closely related to monitoring, and the HOT program does have an environmental monitoring function, the explicit program goals stress scientific understanding: (1) to determine the mechanisms and rates of nutrient input and recycling, especially for N and P, in the upper portion of the water column, (2) to document and understand seasonal and interannual variability in rates of primary production, new production and particle export from the surface ocean, and (3) to measure the time-varying concentrations of carbon dioxide in the upper water column and to estimate the annual air-to-sea gas flux (Karl and Lukas, 1996). Furthermore, without time-series observations there would be little hope of detecting or interpreting links between climate variability and oceanic biogeochemistry.

The fundamental role of nutrient dynamics in biogeochemical processes and ecosystem modeling demands that we have a comprehensive, mechanistic understanding of inventories and fluxes. Although the present study has certainly not resolved all of these important matters it does provide an unprecedented data set to begin the next phase of hypothesis testing. In this phase, it will be essential to design relevant experiments that accommodate the complexity of the entire ecosystem under investigation. Schindler (1998) recently emphasized the need for such ecosystem-scale experiments and has pointed out several problems of scaling the results obtained in micro- or mesocosm studies to an ecosystem level. While it may be difficult, if not impossible, to conduct meaningful, replicated manipulation experiments in the subtropical gyre, the next best approach may be to begin comparisons across different natural ecosystems that are exposed to similar physical perturbations (e.g., ENSO) and, especially, to link investigators at various time-series sites. In particular, biogeochemical modelers will need to work closely with observationalists to gain a better appreciation for oceanic biocomplexity. In any case, long-term data sets are of demonstrable value in ocean research; the global observation network should be expanded.

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