ELSEVIER

Marine Chemistry 56 (1997) 77–96

MARINE CHEMISTRY

Temporal variability in dissolved phosphorus concentrations in the subtropical North Pacific Ocean

David M. Karl, Georgia Tien

SOEST, Department of Oceanography, University of Hawaii, Honolulu, HI 96822, USA

Received 22 November 1995; accepted 22 August 1996

Abstract

Dissolved phosphorus pool measurements were made on approximately monthly intervals during the period October 1988–November 1994 at an oligotrophic, deep-ocean station near Hawaii (Station ALOHA; 22°45′N, 158°W). Data include depth profiles (0–200 m) of soluble reactive phosphorus (SRP), measured by two independent techniques (a high-sensitivity, magnesium-induced coprecipitation (MAGIC) method, and standard autoanalysis procedure), and total dissolved phosphorus (TDP) based on UV photo-oxidation treatment followed by automated SRP analysis. Considerable variability in SRP was observed both with depth and with time over the 6-yr period. Upper water column (0–100 m) SRP concentrations varied in time from > 150 to < 10 nM, and generally conformed to one of two distinct concentration vs. depth patterns: "Type I" profiles were characterized by uniform SRP concentrations with depth (concentration gradients ≤ 0.05 μmol m^{-4} SRP) and "Type II" profiles were characterized by distinct near-surface (0–30 m) SRP concentration maxima. The Type I profiles were further divided into low (Type I-L) or high (Type I-H) categories based on whether the average SRP concentration was < 60 or > 60 nM, respectively. Throughout the entire 6-yr observation period, the upper water column (0–100 m) inventory of SRP displayed a systematic decrease from ~ 10 to ~ 5 mmol m^{-2} P, a result that is consistent with the hypothesized role of N_2 fixation and P control of new and export production at Station ALOHA. Three independent, but not mutually exclusive, models are presented to explain these time-varying SRP concentrations: (1) convective mixing; (2) atmospheric deposition; and (3) upward P flux. The upward P flux model including both passive (upward particle flux) and active (biological transport) processes, is the most consistent model for the available data set.

1. Introduction

Phosphorus (P) is an essential nutrient that, in conjunction with nitrogen (N), controls new and export production in the world's ocean. The relative importance of N vs. P as the export production rate limiting nutrient is probably variable in both time and space (Codispoti, 1989; Karl et al., 1995). Karl et al. (1992) have previously discussed the potential role of biological N_2 fixation as a mechanism to alleviate the chronic N limitation that is believed to exist in the subtropical North Pacific gyre. Although *Trichodesmium* spp. and other microorganisms can fix N_2, the availability of dissolved P or perhaps essential trace elements will ultimately control utilization of this source of new nitrogen. Based on an analysis of the elemental composition of suspended particulate matter and on direct population estimates of *Trichodesmium* spp., Karl et al. (1995) suggested that oceanic conditions attributable to the 1991–1992 El Niño Southern Oscillation (ENSO) event resulted in a biogeochemical shift from a N-limited to a

0304-4203/97/$17.00 Copyright © 1997 Elsevier Science B.V. All rights reserved.
PII S0304-4203(96)00081-3

P-limited habitat with attendant changes in nutrient cycling pathways and rates. With increases in N_2 fixation, a spatial uncoupling of N and P cycles might be expected. In the absence of novel P resupply pathways, a net loss of bioavailable P might be observed over time scales on the order of those equal to the epipelagic P pool residence time (e.g., 1–10 yr). Consequently, detection of these ecosystem changes would require repeated observations over several years.

In the marine environment, dissolved P can exist as free orthophosphoric acid (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$), inorganic polyphosphate and in combination with a variety of organic derivatives, including purines and pyrimidines, sugars and lipids. Both inorganic polyphosphate and most dissolved organic phosphorus (DOP) compounds can be used to satisfy the P requirements of marine bacteria and phytoplankton, albeit at variable rates and efficiencies (Björkman and Karl, 1994). Quantitative analyses of P in seawater have relied on the formation of a *12*-molybdophosphoric acid (*12*-MPA) complex and its subsequent reduction to yield a blue-colored solution, the extinction of which is measured by absorption spectrophotometry (Fiske and Subbarow, 1925; Murphy and Riley, 1962). Strickland and Parsons (1965) first introduced the term "soluble reactive phosphorus" (SRP) and defined it operationally as the phosphorus concentration in a sample that reacts in 5 min with acidified molybdate reagent. Therefore, in addition to free orthophosphate, SRP includes phosphorus that is released from organic or inorganic compounds during the timed reaction period. SRP determinations in low-nutrient seawaters should also be corrected for soluble reactive arsenic (SRAs) interference (Johnson, 1971). Over the years, the term SRP has been used by oceanographers regardless of reaction time or whether a correction for SRAs was made. Consequently, the term SRP is vague, making it difficult to compare measurements between laboratories or across habitats.

In certain marine environments, the soluble nonreactive phosphorus (SNP) pool greatly exceeds the SRP pool, sometimes by up to an order of magnitude (Orrett and Karl, 1987). The SNP pool can be measured following specific, stepwise procedures (e.g., ultraviolet irradiation, enzymatic hydrolysis, high-temperature acid hydrolysis) to convert most combined, non-reactive P compounds to SRP for estimation of the total dissolved phosphorus (TDP) pool. Strickland and Parsons (1972) defined eight separate classes of P compounds based on chemical reactivity. However, it is uncertain which of these compound classes corresponds to the biologically-active phosphorus pool in seawater (Bossard and Karl, 1986; Björkman and Karl, 1994). Despite the availability of these laboratory methods for more than two decades, relatively few data exist for the distributions of the various P-compound classes in the marine environment. At best, SRP and TDP concentrations are measured but more often only SRP, uncorrected for AsO_4^{3-} interference, is reported (e.g., Gordon et al., 1993).

During the U.S.-Joint Global Ocean Flux Study (JGOFS)/World Ocean Circulation Experiment (WOCE)-sponsored Hawaii Ocean Time-series (HOT) research program, established in 1988, a novel method was developed for the precise determinations of SRP at nanomolar concentrations (Karl and Tien, 1992). The method is based on the quantitative removal of SRP from solution by the in vitro formation of brucite ($Mg(OH)_2$), initiated by the addition of NaOH. The brucite precipitate is pelleted by centrifugation and redissolved in HCl prior to formation of the standard *12*-MPA complex. This *mag*nesium-*i*nduced *c*oprecipitation (MAGIC) method has now been used to determine the temporal variability in SRP concentrations in the upper 150 m at the HOT Station ALOHA (22°45′N, 158°W) on approximately monthly intervals for a 6-yr period (1988–1994). The results document a dynamic P cycle that is characterized by the occasional appearance of strong SRP concentration vs. depth gradients in the upper 50–60 m of the water column, near-surface SRP concentration maxima and variable SRP/TDP and SRP/As ratios. These new data for the oligotrophic North Pacific Ocean require a revised paradigm to describe the P cycle in these low-nutrient, open-ocean habitats.

2. Materials and methods

2.1. Site location and sampling

All samples were collected at Station ALOHA (A Long-term Oligotrophic Habitat Assessment) within

a 6-n.mi. radius of the nominal site at 22°45′N, 158°W (Fig. 1) during approximately monthly research cruises (Karl and Lukas, 1996). Station ALOHA is positioned in deep water (> 4700 m) ~ 100 km due north (upwind) of the Hawaiian Islands. The surface waters at Station ALOHA are characterized by low nutrients and low standing stocks of photosynthetic microorganisms (Letelier et al., 1993). The time-series data set reported in this paper began with HOT-1 in October 1988 and ended with HOT-59 in November 1994 (Table 1). The HOT program is an ongoing program with sampling planned, at least, through July 1998.

Each 5-day HOT program cruise collects high-resolution continuous environmental data using a Sea Bird CTD and associated sensor packages. A General Oceanics 24-place rosette with 24 12-liter polyvinylchloride (PVC) bottles is used to collect water. Numerous basic measurements are routinely made including a variety of physical and chemical determinations, as well as selected biological rate measurements (Karl and Winn, 1991; Karl and Lukas, 1996). This paper focuses on the observed temporal variations in SRP and TDP concentrations.

2.2. SRP *measurements*

Seawater for SRP determinations was subsampled directly from the PVC sampling bottles into either 125- or 500-ml high-density polyethylene (HDPE) storage bottles that had been acid-washed (1 *M* HCl) and deionized–distilled water (DDW) rinsed before use. Each bottle was rinsed three times with sample before final water collection. The bottles were filled ~ $\frac{2}{3}$ full and placed upright in a −20°C freezer. Frozen samples remained in the dark, typically for several days prior to analysis at which time they were completely thawed at room temperature or in a water bath and brought to ambient laboratory temperature. These collection and storage procedures have been shown to be ideal for nutrient measurements in oligotrophic seawaters (Dore et al., 1996). SRP concentrations were measured by two independent methods: (1) automated flow analysis and (2) MAGIC, followed by manual spectrophotometric determination.

The automated SRP analyses were carried out using a 4-channel continuous flow Technicon Autoanalyzer II according to manufacturer's recommen-

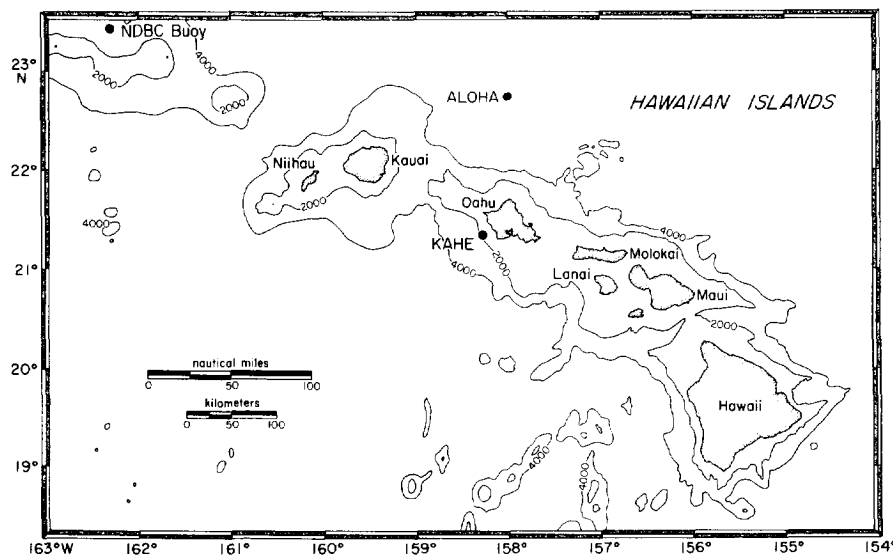


Fig. 1. Location of Station ALOHA, depth contours are in meters. Station ALOHA is defined as the region in a 6-n.mi.-radius circle around 22°45′N, 158°W.

Table 1
Chronology of Hawaii Ocean Time-series (HOT) cruises for the period 1988–1994

HOT Cruise No.	Dates	SRP profile type [a]	Maximum SRP concentration [b] (n*M*)	Depth of SRP maximum (m)
1	29 Oct.–3 Nov. 1988	II	37	10
2	30 Nov.–4 Dec. 1988	I-L	43	62
3	6 Jan.–10 Jan. 1989	I-L	45	77
4	24 Feb.–28 Feb. 1989	II	122	25
5	25 Mar.–29 Mar. 1989	II	144	5
6	16 May–20 May 1989	I-H	69	17
7	22 Jun.–26 Jun. 1989	II	152	5
8	27 Jul.–31 Jul. 1989	– [c]	–	–
9	22 Aug.–26 Aug. 1989	I-H	107	100
10	21 Sep.–24 Sep. 1989	I-H	109	25
11	16 Oct.–20 Oct. 1989	I-H	88	44
12	26 Nov.–29 Nov. 1989	–	–	–
13	3 Jan.–7 Jan. 1990	I-L	60	1
14	13 Feb.–17 Feb. 1990	I-H	131	26
15	17 Mar.–21 Mar. 1990	–	–	–
16	11 Apr.–15 Apr. 1990	I-H	114	15
17	7 May–11 May 1990	I-H	132	44
18	11 Jun.–15 Jun. 1990	I-H	90	5
19	23 Jul.–27 Jul. 1990	–	–	–
20	13 Sep.–17 Sep. 1990	II	117	20
21	17 Nov.–20 Nov. 1990	–	–	–
22	16 Dec.–20 Dec. 1990	I-H	130	60
23	1 Feb.–6 Feb. 1991	II	126	5
24	5 Mar.–9 Mar. 1991	I-H	78	36
25	8 Apr.–12 Apr. 1991	II	55	8
26	6 May–10 May 1991	II	83	7
27	3 Jun.–6 Jun. 1991	II	128	5
28	8 Jul.–12 Jul. 1991	I-H	147	23
29	8 Aug.–12 Aug. 1991	II	162	26
30	16 Sep.–20 Sep. 1991	I-H	104	4
31	19 Oct.–24 Oct. 1991	I-L	39	25
32	4 Dec.–9 Dec. 1991	II	86	22
33	3 Jan.–8 Jan. 1992	II	38	25
34	12 Feb.–17 Feb. 1992	I-L	34	34
35	3 Mar.–8 Mar. 1992	II	82	15
36	15 Apr.–20 Apr. 1992	II	110	5
37	7 Jun.–11 Jun. 1992	II	89	5
38	3 Jul.–7 Jul. 1992	II	26	24
39	3 Aug.–8 Aug. 1992	II	117	24
40	20 Sep.–25 Sep. 1992	I-L	29	16
41	17 Oct.–22 Oct. 1992	II	26	6
42	23 Nov.–25 Nov. 1992	I-H	123	15
43	15 Dec.–17 Dec. 1992	II	119	5
44	18 Jan.–22 Jan. 1993	I-L	48	11
45	15 Feb.–20 Feb. 1993	I-H	85	15
46	12 Apr.–17 Apr. 1993	I-H	76	4
47	18 May–23 May 1993	I-L	34	44
48	26 Jul. 1993	–	–	–
49	9 Sep.–17 Sep. 1993	II	48	15
50	27 Oct.–1 Nov. 1993	I-L	58	26
51	18 Jan.–23 Jan. 1994	I-H	67	26

Table 1 (continued)

HOT Cruise No.	Dates	SRP profile type [a]	Maximum SRP concentration [b] (n*M*)	Depth of SRP maximum (m)
52	15 Feb.–20 Feb. 1994	I-L	21	15
53	7 Mar.–12 Mar. 1994	II	38	46
54	17 Jun.–22 Jun. 1994	II	62	25
55	23 Jul.–28 Jul. 1994	I-L	54	60
56	28 Aug.–2 Sep. 1994	I-L	57	15
57	21 Sep.–26 Sep. 1994	I-L	58	5
58	13 Oct.–18 Oct. 1994	II	21	25
59	17 Nov.–22 Nov. 1994	I-L	37	15

[a] Type I and Type II profiles are characterized by the presence or absence of a near-surface enrichment of SRP with a concentration gradient of ≤ 0.05 μmol m^{-4} SRP for Type I profiles and > 0.05 μmol m^{-4} SRP for Type II profiles. Type I-L and Type I-H are arbitrarily defined as uniform SRP concentration vs. depth profiles with mean surface water (0–100 m) SRP concentration less than (Type I-L) or greater than (Type I-H) 60 n*M*.

[b] Maximum SRP concentration in upper 100 m of the water column for Type I profiles or in the surface enriched zone for Type II SRP profiles

[c] SRP-M samples not collected.

dations with slight modifications to surfactant concentrations, sampling rate and pump tubing diameter (T. Walsh, SOEST Analytical Services, pers. commun.). The autoanalyzer SRP colorimetric detection is based on the standard molybdenum blue procedure (Strickland and Parsons, 1972). DDW is used as the diluent for all reagents and to establish the instrument response baseline. Seawater refractive index and turbidity blanks are used as corrections. For the low SRP concentrations reported in this study (≤ 400 n*M*) we estimate the precision to be $\sim \pm 20$ n*M* and hence the detection limit is ~ 40 n*M*. No SRAs correction was attempted for the automated SRP analyses. Dissolved phosphorus concentrations estimated using this autoanalyzer procedure are hereafter referred to as "SRP-AA".

Subsamples for MAGIC treatments (typically 6 replicates, 50 ml each) were decanted into disposable 50-ml polypropylene centrifuge tubes. High-purity NaOH (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, and mixed vigorously then centrifuged ($1000 \times g$; 60 min) to pellet the insoluble $Mg(OH)_2$ containing the adsorbed P and As. Under these reaction conditions, PO_4^{3-} and inorganic polyphosphate are quantitatively removed, but DOP is only partially scavenged. Following centrifugation, the supernatant is removed by vacuum aspiration and the pellet is dissolved in 10 ml of high-purity 0.1 *M* HCl. At this point, three of the six subsamples are analyzed for [SRP + SRAs] using the standard molybdenum blue color reaction (Karl and Tien, 1992), and the remaining three replicates are treated to eliminate AsO_4^{3-} reactivity (see below). The treated samples are then assumed to measure SRP only, and the difference between the treated and untreated samples is an estimate of the AsO_4^{3-} concentration (see below). As described, the reliable detection limit for MAGIC is ~ 2–3 n*M* with an average precision of $\pm 5\%$ for samples with SRP concentrations in the range of 10–50 n*M*. Above 50 n*M* the precision is generally ± 2–3%. The AsO_4^{3-} corrected phosphorus concentrations estimated using the MAGIC procedure as described above are hereafter referred to as "SRP-M".

2.3. Arsenate measurements

Arsenate (AsO_4^{3-}) reacts with the SRP reagents and forms a blue-colored complex of an equivalent molar absorptivity to that of PO_4^{3-}, while arsenite (AsO_3^{3-}) does not react at all. Dissolved AsO_4^{3-} can be reduced to AsO_3^{3-} with thiosulfate in acidic medium in the presence of excess metabisulfate (von Schouwenburg and Walinga, 1967). Because the time for color development is prolonged by the addition of thiosulfate required to eliminate AsO_4^{3-} interference, this correction is not routinely employed in

most automated SRP analyses (Downes, 1978). Arsenate has been shown to be concentrated along with SRP using the MAGIC procedure described above and reduced by thiosulfate (data not shown). By combining the MAGIC procedure and thiosulfate reduction, we have obtained accurate and precise determinations of both SRP and AsO_4^{3-}. The difference in concentration between treated and untreated samples, relative to appropriate P standards, is a measure of AsO_4^{3-} concentration (Johnson, 1971). This analytical approach assumes that SRP and SNP are unaffected by the thiosulfate treatment, and also assumes that all As reactivity in the treated samples is a result of AsO_4^{3-}. Like all concentration difference measurements, the precision of AsO_4^{3-} estimation by this method decreases as SRP concentration increases. For samples collected in the upper portion of the water column at Station ALOHA, the precision ranged from 3% to 20%, and was typically $\pm 10\%$.

2.4. TDP *measurements and* SNP *estimation*

Routine measurements of TDP were obtained by treatment of a 30-ml subsample contained in a quartz tube to ultraviolet light photo-oxidation (2 h, 1200-W lamp at 84 ± 6°C), as described by Armstrong et al. (1966) followed by autoanalysis of the hydrolysis products using standard procedures for SRP-AA determination (see above). Certain P-containing compounds (e.g., inorganic polyphosphates and phosphonates) are not completely hydrolyzed under these conditions. However, these compound classes are not expected to comprise a significant portion of the TDP pool under the low-nutrient conditions observed at Station ALOHA (Solorzano and Strickland, 1968; Ridal and Moore, 1990). Like the SRP-AA determinations, TDP estimates were not corrected for total dissolved arsenic (TDAs, i.e. AsO_4^{3-} plus AsO_4^{3-} released from organic complexes or produced via oxidation of AsO_3^{3-}). Consequently, we estimate SNP concentrations by subtracting the SRP-AA values (as opposed to the SRP-M determinations) from TDP. The typical precision of SNP estimation by this method was $\pm 15\%$ for TDP values ranging from 100 to 400 n*M*. MAGIC-based TDP estimation was not attempted in this study.

3. Results and discussion

3.1. *Comparison of* SRP − AA *and* SRP − M *methods*

A summary comparison of the standard autoanalyzer method to the MAGIC procedure for SRP determinations in the surface waters at Station ALOHA revealed several interesting observations and robust trends. The combined 42-cruise, 301 paired sample data set demonstrated that the two methods, on average, yielded similar SRP concentration estimates for water samples collected in the upper 150 m of the water column where SRP concentrations ranged from < 20 to > 300 n*M* (Fig. 2). The difference between the two independent measurements (calculated as [SRP-AA] − [SRP-M]) is not significantly different from zero ($\bar{x} = 2.42$ n*M*, $s = 30.0$ n*M*, $n = 301$).

The actual difference between these two analytical methods for a given sample pair, however, is not random but reflects what we believe to be changes in the chemical composition of the SRP or TDP pools (or both). For example, on selected cruises (e.g., HOT-14 and -18; Fig. 3, top) we observed SRP-AA and SRP-M concentration profiles that were indistinguishable. On other cruises there were systematic offsets between the two independent SRP estimates, that were restricted to the upper portion of the water column (Fig. 3, center and bottom). When SRP differences were observed, the MAGIC procedure generally yielded lower SRP concentration estimates (e.g., Fig. 3, center). However, on isolated cruises SRP-AA was lower than SRP-M estimates (Fig. 3, bottom). Because these two independent procedures were conducted in separate laboratories and by different analysts we initially considered that operator differences, including but not limited to the use of separate reference standards, might have contributed to these results. However, this would not explain the majority of the profiles where the two SRP estimates are different for one portion of the depth profile but identical elsewhere (Fig. 3, center and bottom). We suggest that these SRP concentration differences are a result of depth-specific variations in the chemical composition of the TDP pools, changes in the relative reactivity of the SRP in selected samples or a manifestation of AsO_4^{3-} interference.

In the hypothetical case where the TDP pool is comprised entirely of SRP in the form of orthophosphate, one would expect excellent agreement between the two methods of analysis. However, for "real world" samples where the SRP pool is a small percentage of the total P pool and contains both orthophosphate and acid-labile organic phosphorus as well as AsO_4^{3-}, there is an a priori reason to expect the two methods to deviate significantly in their estimates of SRP concentrations. For example, if acid-labile phosphate esters are present in the water sample, then the standard, acidic automated colorimetric procedures would be expected to yield SRP concentrations that are greater than those measured using the MAGIC procedure. This prediction derives from the fact that during the selective concentration of orthophosphate in the MAGIC procedure, using the reagent concentrations employed in this study, most organic phosphorus compounds would remain in the alkaline supernatant during the isolation of $Mg(OH)_2$ and would not be subjected to acid hydrolysis. On the other hand, variations in the TDP pool composition could also cause the MAGIC procedure to yield higher SRP values than observed with the standard automated analysis if, for example, alkaline-labile P-containing organic compounds were present. All three of these possibilities (i.e. SRP-AA = SRP-M, SRP-AA > SRP-M and SRP-AA < SRP-M) are observed at Station ALOHA during the first six years of the HOT program (Fig. 3). At the present time, it is impossible to know which of these two methods provides the more reliable estimate of the biologically-available phosphorus pool, the component of greatest interest in studies of P cycling in the marine environment (Bossard and Karl, 1986; Orrett and Karl, 1987; Karl and Yanagi, 1996).

3.2. Variability in concentration profiles and upper water column inventories of phosphorus

SRP-M concentration profiles at Station ALOHA varied considerably but systematically during the

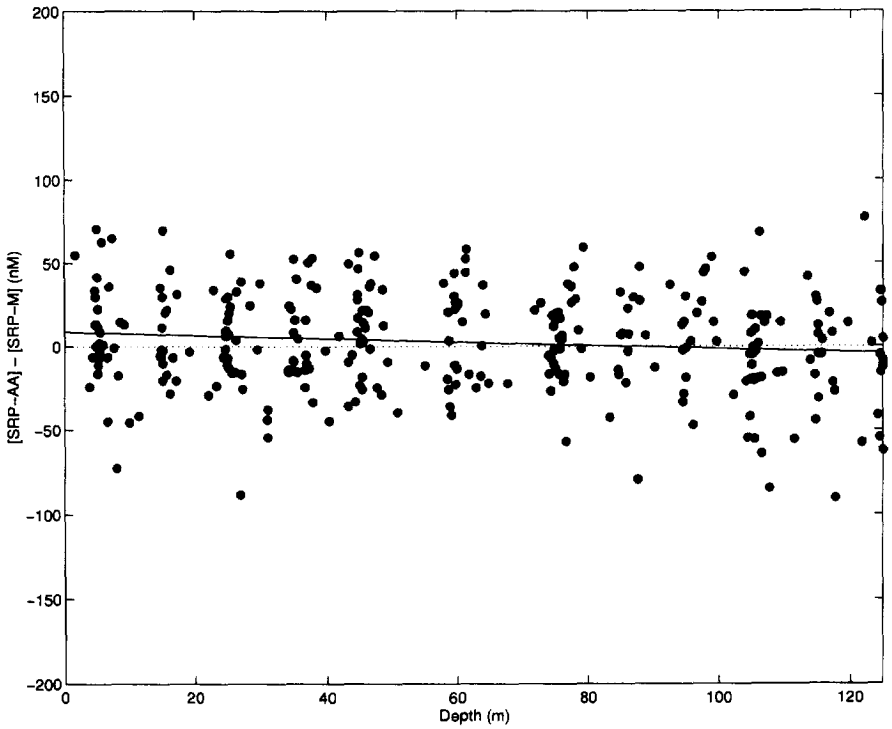


Fig. 2. Comparison of SRP estimates for replicate water samples measured using autoanalyzer (AA) and MAGIC (M) techniques. The plot shows the concentration difference calculated as [SRP-AA] – [SRP-M], for each of the 301 paired sample comparisons, as a function of depth. Mean SRP estimates ranged from < 20 to > 300 nM. The slope of the model I linear regression analysis (*solid line*; $y = -0.1018x + 8.6$) is not significantly different from zero (dashed line).

6-yr period of observation (Fig. 4). At least two distinct profile classes were observed. The first, referred to as "Type I SRP-M" profiles, were characterized by uniform SRP concentrations with depth (concentration gradients ≤ 0.05 μmol m^{-4} SRP) over the upper 100 m of the water column (Fig. 4, left). Despite the similarities in profile structure, the average SRP concentrations ranged from < 20 nM on HOT-52 (February 1994) to > 110 nM on HOT-42 (November 1992), resulting in different upper water column SRP inventories. We have arbitrarily divided these Type I SRP-M profiles into low-concentration (Type I-L; SRP-M ≤ 60 nM) and high-concentration (Type I-H; SRP-M > 60 nM) profiles on the basis of mean SRP concentrations (Table 1; Fig. 4, left).

The second distinct class, referred to as "Type II SRP-M" profiles, is characterized by elevated near-surface (0–30 m) concentrations of SRP relative to mid-euphotic zone (40–80 m) SRP concentration minima (Fig. 4, right). The near-surface SRP maxima ranged in concentration from < 60 nM on

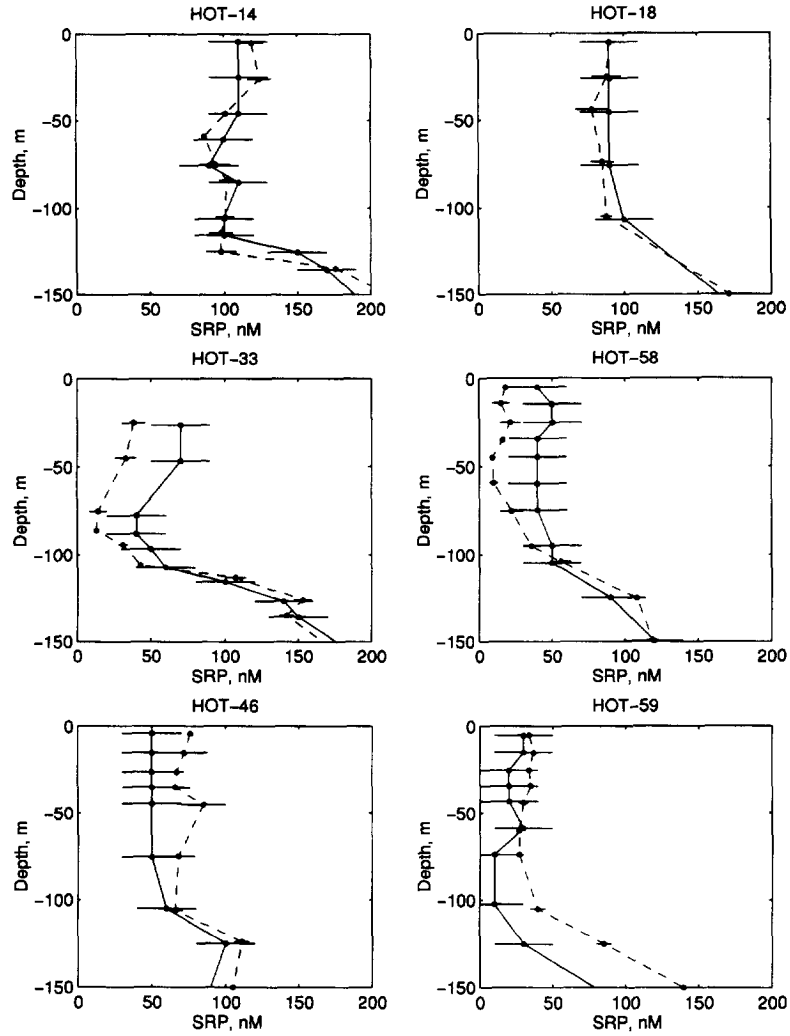


Fig. 3. Selected SRP concentrations vs. depth at Station ALOHA. Data shown are: *dashed line* = mean ± 1 standard deviation ($n = 3$) for SRP-M determinations; and *solid line* = SRP-AA measurements with the estimated error (±20 nM) shown. Three distinct patterns are observed: (1) SRP-AA = SRP-M; (2) SRP-AA < SRP-M; and (3) SRP-AA > SRP-M. The cruise dates are given in Table 1.

HOT-25 (April 1991) to ~ 130 n*M* on HOT-14 (February 1990). These maximum values are mostly within the range of the SRP-M concentrations measured for the Type I-H profiles (Fig. 4, left). Furthermore, the typical Type II profile SRP minima are similar to the average Type I-L profile SRP concentrations. Consequently, one could explain the formation of a Type II SRP-M distribution as either a surface SRP enrichment superimposed on an existing Type I-L profile or as the mid-euphotic depth removal of SRP from a Type I-H concentration profile (Fig. 4).

During our ~ 6-yr period of observation, the temporal variability of SRP-M concentrations during the 13-month interval from April 1992 to May 1993 deserves special attention. This period of time coincided with the 1991–1993 ENSO period with a hypothesized shift from a N-limited to a P-limited ecosystem at Station ALOHA (Karl et al., 1995). SRP data obtained during ENSO revealed a recurrent 3-month pattern of change from Type I-H, through Type II to a Type I-L profile (Fig. 5). We believe that these four independent and clearly resolved "cycles" cannot easily be dismissed as coincidence and must have an underlying mechanistic cause, perhaps related to the ENSO event itself. In contrast to these cyclic patterns and large coherent fluctuations in the upper water column SRP-M concentrations, the corresponding SNP profiles showed no systematic trends that might imply the production of SRP from SNP (Fig. 6). The physical and biological processes potentially contributing to these implied SRP cycles will be discussed in Section 3.4.

The 6-yr trends in the upper ocean (0–100) inven-

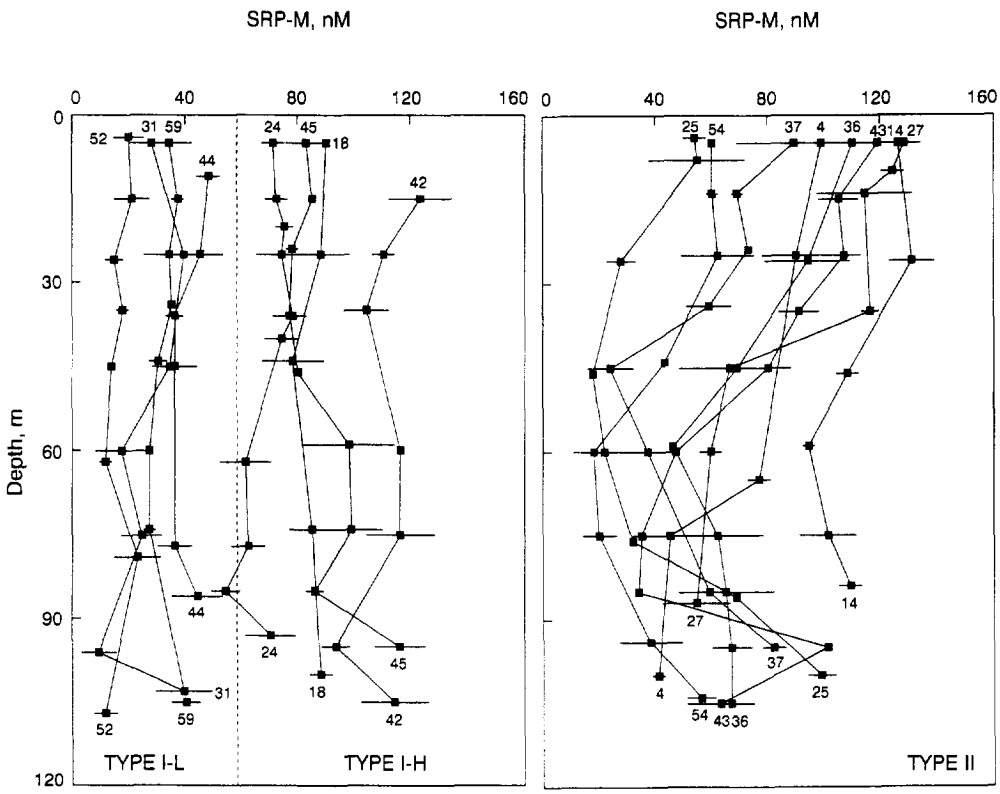


Fig. 4. Selected SRP-M concentrations vs. depth at Station ALOHA showing two different profile patterns: [LEFT] Type I profiles displaying a relatively constant SRP concentration vs. depth; and [RIGHT] Type II profiles displaying near-surface enrichments of SRP, relative to mid-euphotic zone concentrations. The *number* above and below each profile indicates the HOT cruise on which each data set was collected; cruise dates are given in Table 1. The data shown are the mean values ±1 SD ($n = 3$).

tories of SRP-AA, SRP-M and SNP reveal large and decoupled interannual variability (Figs. 7 and 8). The most dramatic features of this time-series data set are: (1) systematic and sustained decreasing inventories for both SRP-AA and SRP-M during the entire period of observation from values of ~ 10 mmol m^{-2} in January 1989 to ~ 5 mmol m^{-2} in December 1994; (2) periods of covariation of SRP-AA and SRP-M alternating with periods of large concentration differences between these two independent measures of SRP (the differences are most apparent during the 1991–1992 ENSO period); (3) a sustained net accumulation of SNP over the entire period of observation from ~ 19 mmol m^{-2} P in January 1989 to ~ 26 mmol m^{-2} P in December 1994; and (4) periods of large SNP pool concentration fluctua-

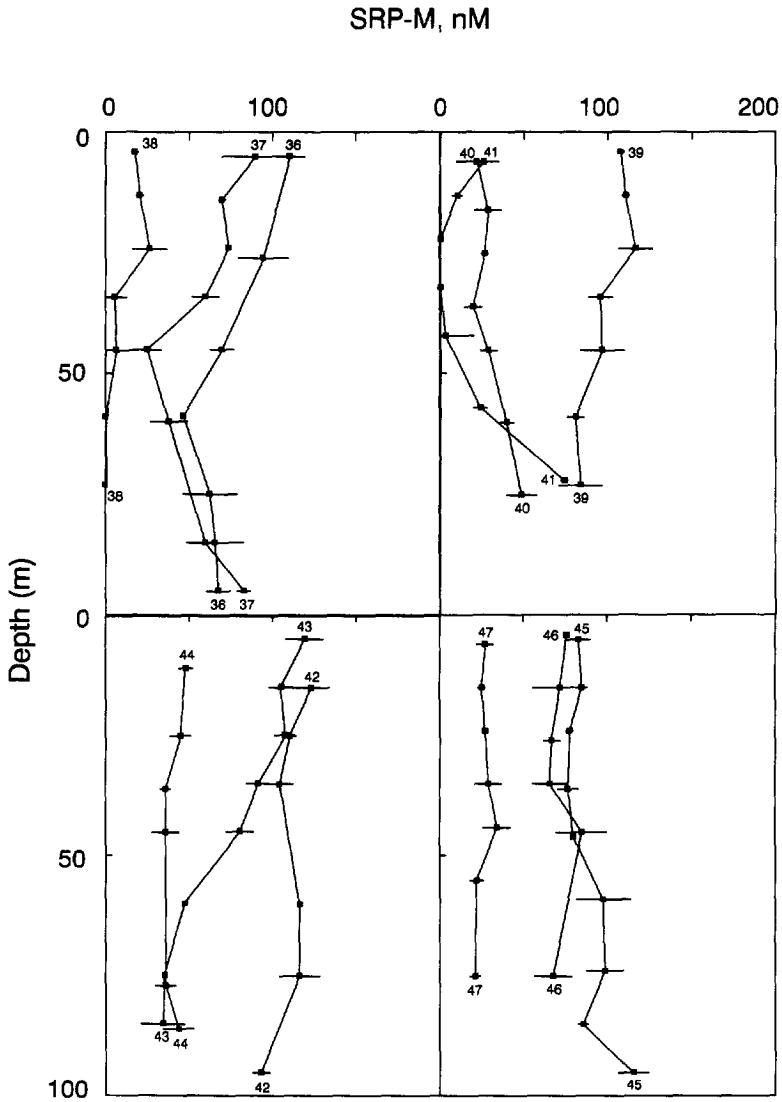


Fig. 5. SRP-M concentration vs. depth at Station ALOHA for 12 consecutive HOT cruises between April 1992 and May 1993. The *number* above and below each profile indicates the HOT cruise on which each data set was collected; cruise dates are given in Table 1. The data shown are the mean values ± 1 SD ($n = 3$). On HOT-38 and HOT-41, the several mid-euphotic zone concentrations plotted on the x-axis were indistinguishable from zero.

tion (sustained net accumulation, followed by sustained net removal), especially during the 1991–1992 ENSO event (Fig. 8). During this entire period of observation, the HOT program quality control charts for SRP determinations at three specific density surfaces that are routinely tracked (all below 1000 m) were all within acceptable limits (±5%, Fig. 9) indicating that there were no serious measurement or standarization problems. Consequently, we are confident that the systematic changes in SRP and SNP inventories in the upper water column reflect the true ecosystem trends.

By comparison to these dissolved P pools, the depth-integrated (0–100 m) particulate phosphorus (PP) pools ranged from 1.5–2.5 mmol m^{-2} P with no systematic variation over the 6-yr period of observation (data not shown). On the basis of these results we conclude that SRP and SNP pool dynamics are independent of the PP pool, or at the very least decoupled, on time scales up to 6 yr.

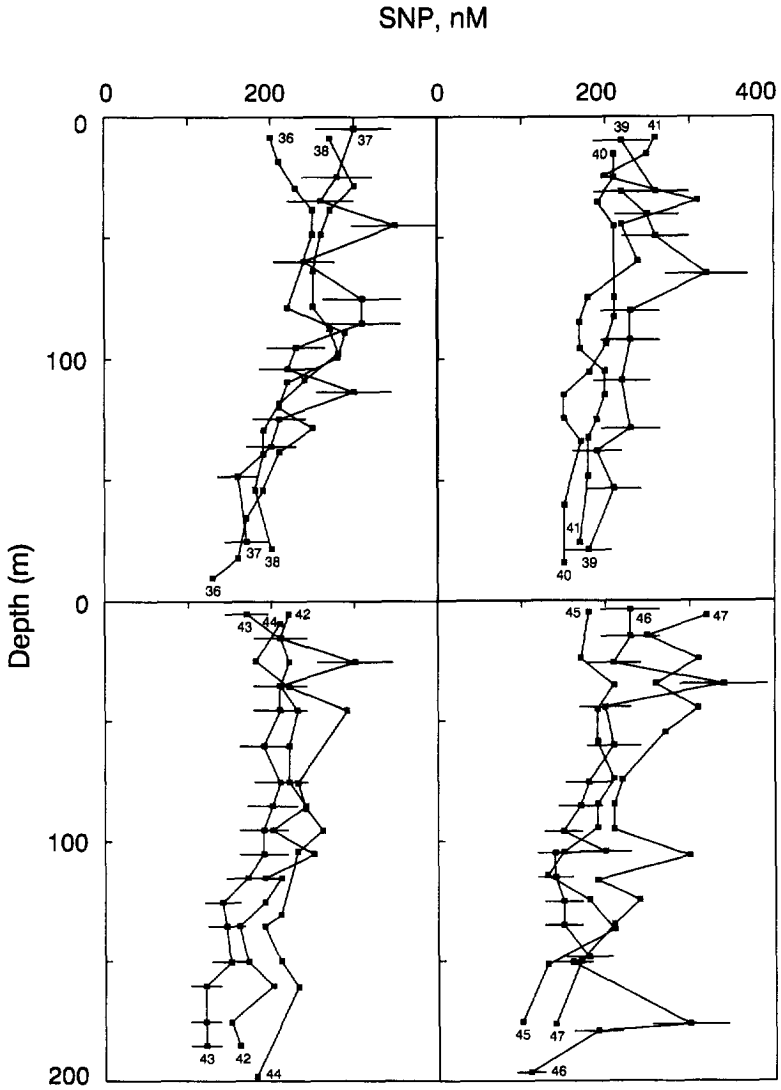


Fig. 6. SNP concentration vs. depth at Station ALOHA for the 12 cruises shown in Fig. 5. The data shown are mean values; for clarity of presentation, representative coefficients of variation (CV = 15%) are given for only 1 profile in each set.

The accumulation of SNP during the ENSO period is especially intriguing considering independent evidence suggesting that the habitat near Station ALOHA was P-limited during this period of time (Karl et al., 1995). It appears that SRP, rather than SNP, is the more reliable estimate of biologically-available phosphorus during the ENSO period. If this interpretation is correct, then one must invoke either the in situ production and accumulation of relatively refractory SNP compounds or a net flux of SNP to the surface waters from elsewhere, for example, atmospheric deposition or upward transport from the subeuphotic zone habitat.

Although the long-term SRP decrease and corresponding SNP increase partially offset each other and serve to dampen the TDP pool dynamics, we do observe a net accumulation in the 0–100-m-integrated TDP during the 6-yr period of 0.44 mmol m^{-2} yr^{-1} P. This observed P accumulation rate is < 10% of the mean downward P flux at the 150-m reference level (5.2 mmol m^{-2} yr^{-1} P), as measured using free-drifting sediment traps (Karl et al., 1996). During this same period, the total dissolved nitrogen (TDN) pool increased at an average rate of 19.6 mmol m^{-2} yr^{-1} N, and the mean downward N flux at the 150-m reference level was 112 mol m^{-2} yr^{-1} N (Karl et al., 1996). The mean N/P (mol/mol) ratio of 45:1 for the dissolved pool is nearly three times greater than that typically observed in marine plankton (Redfield et al., 1963). This observed accumulation of N-enriched organic matter is consistent with other independent lines of evidence for increased N_2-fixation activity during this period of observation (Karl et al., 1995; Letelier and Karl, 1996).

Finally, the implied accumulation of dissolved organic carbon (assuming a C/N molar ratio of 20:1 for Station ALOHA dissolved organic matter; Karl et al., 1993) is 392 mmol m^{-2} yr^{-1} C, or an average increase of 3.92 mmol m^{-3} yr^{-1} C. This rate of increase of dissolved organic matter is greater than half of the annual net air-to-sea flux of carbon dioxide (~ 700 mmol m^{-2} yr^{-1}; Winn et al., 1994) measured at Station ALOHA. Because the implied increase in dissolved inorganic carbon (DIC) of 10 mmol m^{-3} yr^{-1} (average increase for upper 75 m)

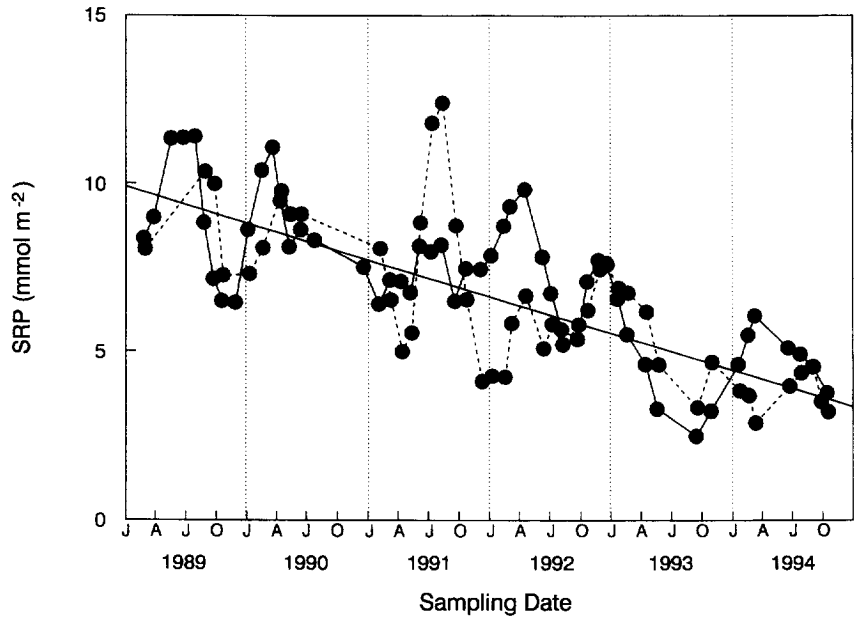


Fig. 7. Time-series of depth-integrated (0–100 m) phosphorus inventories at Station ALOHA for the period 1989–1994. The data points are 3-point running mean values for either SRP-AA (*solid line*) or SRP-M (*dashed line*). The model I linear regression fit for the SRP-M data set is: SRP-M (mmol m^{-2}) = 9.95 − [0.003 × (days since 1 Jan. 1989)].

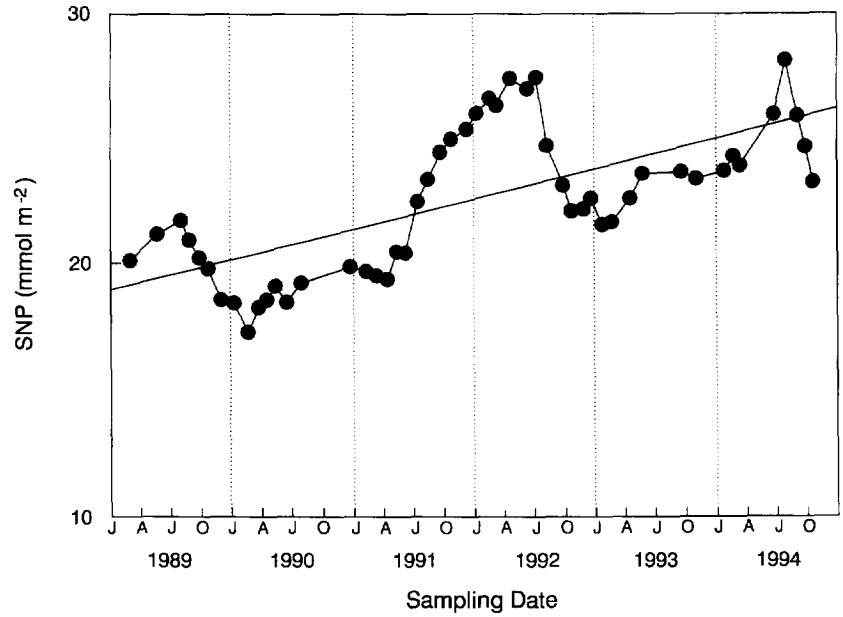


Fig. 8. As in Fig. 7. except for soluble non-reactive phosphorus (SNP) pool. The model I linear regression fit is: SNP (mmol m^{-2}) = 18.98 + [0.0033 × (days since 1 Jan. 1988)].

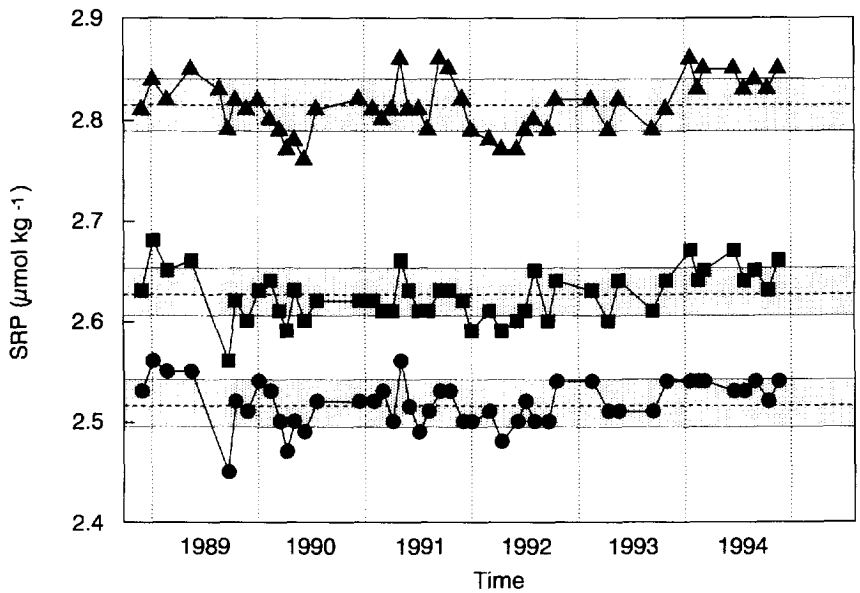


Fig. 9. HOT program quality control/assurance plot for the measurements of soluble reactive phosphorus (SRP-AA) at three reference potential density horizons (● = 27.675; ■ = 27.758; ▲ = 27.782) for the first 6 years of field measurement. The *dashed lines* and *shaded regions* show the mean and ± 1 standard devation intervals for each data set.

was not detected in the long-term data set, Winn et al. (1994) concluded that the "extra" carbon must be removed from the region by Ekman-driven downwelling processes. However, with consideration of the new data presented here, it is probable that a significant portion of the "missing" DIC has simply been transformed to dissolved organic matter that is, for unknown reasons, accumulating over these fairly long time scales in the upper water column. Clearly, this accumulation must be viewed as a non steady-state condition of the subtropical gyre, and this trend may be unique to the 1989–1994 period. It is quite possible that this feature is itself a consequence of N_2 fixation and the alternation from N limitation to P limitation (Karl et al., 1995).

3.3. Arsenate distributions and SRP/As ratios

Arsenic is present in the marine environment as dissolved AsO_4^{3-}, AsO_3^{3-} and as mono-, di- and trimethylarsenic acids, and is also present in living organisms in a variety of organoarsenical compounds (Gorgy et al., 1948; Andreae, 1978, 1979; de Bettencourt, 1988; Anderson and Bruland, 1991). An authoritative review of biotransformation of As by marine organisms has recently appeared (Francesconi and Edmonds, 1993). Direct measurements in the North Atlantic (Johnson and Pilson, 1972) and North Pacific Oceans (Andreae, 1978) have demonstrated that AsO_4^{3-} is the dominant form of arsenic in seawater. Nevertheless, AsO_3^{3-} is generally found at concentrations greater than those predicted from thermodynamic calculations (Johnson and Pilson, 1972). Selected marine microorganisms are able to reduce and oxidize various forms of inorganic As and to produce methylated derivatives (Johnson, 1972; Andreae, 1978; Johnson and Burke, 1978; Benson, 1984). In the present study, only AsO_4^{3-} concentrations were measured.

In contrast to the dynamic variations observed for SRP-M concentrations in the upper water column at Station ALOHA, AsO_4^{3-} was relatively invariant in time and with depth. For example, we did not observe surface AsO_4^{3-} enrichments in any of the cruises that displayed Type II SRP-M profiles. Furthermore, during time intervals of implied net SRP removal from the water column the water column AsO_4^{3-} inventories were invariant (Table 2). Consequently, the SRP/As molar ratios varied considerably at our study site (Table 2).

These AsO_4^{3-} results are of general interest for several reasons. First, the two major sources of As for the upper ocean are atmospheric deposition (Walsh et al., 1979) and upwelling (Johnson and Pilson, 1972; Andreae, 1979). Because AsO_4^{3-} is incorporated into living organisms there is net removal from surface waters and net regeneration below the euphotic zone and full ocean depth profiles of AsO_4^{3-} display these expected concentration vs. depth trends (Andreae, 1978). Nevertheless, if the fluctuating SRP levels that we observe at Station ALOHA are the result of deep mixing processes, then we would have expected a covariation of near-surface ocean AsO_4^{3-} concentrations, which we did not see in this study. With regard to atmospheric deposition processes, the same covariance would be observed if this pathway was responsible for the major flux of both elements. Of course, with different residence times the dynamics of the soluble pools are expected to vary independently, as they apparently do.

Second, the ratio of SRP/As is of importance because of the well-documented competitive inhibition of AsO_4^{3-} on microbial PO_4^{3-} uptake (Button et al., 1973). The previously mentioned microbiological transformations of AsO_4^{3-} to AsO_3^{3-} and to the various known methylated derivatives may be a mechanism to reduce As toxicity (Benson, 1984). If the plankton populations at Station ALOHA are also susceptible to AsO_4^{3-} inhibition, then one must question how algal and bacterial metabolism continue to function with molar SRP/As ≤ 0.1 (Table 2). We see no consistent pattern that could be interpreted as in situ AsO_4^{3-} toxicity or AsO_4^{3-} detoxification (i.e. reduction in ambient pool) even when SRP-M levels approached our analytical detection limit of 2–3 n*M* (Table 2). Either the microorganisms in the surface waters near Station ALOHA have an unusually high tolerance for AsO_4^{3-}, or the SNP pool serves as the primary source of P under these conditions, thereby providing an acceptable P "buffer" to the presence of this potent metabolic inhibitor. In that regard, the TDP/As ratios are generally > 10 for the surface waters at Station ALOHA (Table 2).

Finally, if physical processes such as adsorption onto particles coupled to gravitational settling are

important for the mid-euphotic zone depth removal of SRP (e.g., Type II SRP-M profiles), then we might expect to observe similar SRAs concentration vs. depth trends because of similar chemical behavior but we did not. Although this does not completely rule out particle scavenging as a potentially important SRP removal mechanism, it does provide additional constraints.

3.4. *Surface* SRP − M *enrichment hypotheses*

One of the most interesting and potentially important observations from our 6-yr data set is the pres-

Table 2
Selected results of soluble reactive phosphorus and arsenate concentrations for Station ALOHA as determined by the MAGIC technique

Cruise No. (date)	Depth (m)	SRP-M [a] (n*M*)	AsO_4^{3-} [b] (n*M*)	SRP/As (mol/mol)	TDP [c] (n*M*)	TDP/As (mol/mol)
H-36	5	110 (±9)	20 (±3)	5.50	200 (±30)	10.0
(April 1992)	26	94 (±15)	21 (±2)	4.48	230 (±35)	11.0
	45	69 (±7)	19 (±2)	3.63	250 (±38)	13.2
	59	46 (±1)	30 (±3)	1.53	–	–
	75	62 (±16)	30 (±5)	2.07	220 (±33)	7.33
	85	65 (±17)	22 (±4)	2.95	290 (±44)	13.2
	95	67 (±7)	17 (±1)	3.94	280 (±42)	16.5
	105	67 (±4)	18 (±1)	3.72	220 (±33)	12.2
	115	88 (±6)	25 (±2)	3.52	210 (±32)	8.40
	126	118 (±2)	18 (±1)	6.56	250 (±38)	13.9
	135	147 (±7)	23 (±1)	6.39	210 (±32)	9.13
	150	273 (±6)	24 (±1)	11.4	190 (±28)	7.92
	177	352 (±8)	15 (±1)	23.5	170 (±26)	11.3
	199	450 (±28)	19 (±1)	23.7	150 (±23)	7.89
H-37	5	89 (±20)	12 (±2)	7.42	300 (±45)	25.0
(June 1992)	14	69 (±2)	23 (±2)	3.00	–	–
	24	73 (±1)	21 (±2)	3.48	280 (±42)	13.3
	34	59 (±8)	11 (±1)	5.36	260 (±39)	23.6
	45	24 (±8)	17 (±2)	1.41	350 (±53)	20.6
	60	37 (±11)	15 (±2)	2.47	240 (±36)	16.0
	85	59 (±10)	26 (±3)	2.27	310 (±47)	11.9
	95	82 (±4)	20 (±1)	4.10	230 (±35)	11.5
	114	111 (±3)	28 (±2)	3.96	300 (±45)	10.7
	125	130 (±9)	29 (±1)	4.48	210 (±32)	7.24
	148	254 (±7)	16 (±1)	15.9	160 (±24)	10.0
	175	436 (±4)	10 (±1)	43.6	170 (±26)	17.0
	202	634 (±17)	26 (±1)	24.4	150 (±23)	5.77
H-38	4	17 (±2)	24 (±2)	0.71	270 (±41)	11.3
(July 1992)	13	20 (±2)	26 (±1)	0.77	–	–
	34	5 (±7)	18 (±2)	0.28	270 (±41)	15.0
	45	6 (±12)	16 (±3)	0.38	260 (±39)	16.3
	59	< 3	19 (±2)	< 0.1	250 (±38)	13.2
	73	< 3	21 (±5)	< 0.1	250 (±38)	11.9
	124	53 (±2)	20 (±1)	2.65	190 (±28)	9.5
	174	168 (±5)	11 (±1)	15.3	200 (±30)	18.2
	196	221 (±4)	18 (±1)	12.3	160 (±24)	8.89

[a] Mean ± 1 standard deviation ($n = 3$), after treatment to reduce AsO_4^{3-} to AsO_3^{3-} (Johnson, 1972).

[b] Mean ± 1 standard deviation ($n = 3$) calculated as the difference between paired, triplicate sample sets with and without AsO_4^{3-} reduction treatment. The AsO_4^{3-} values were estimated as: $(A \pm a) - (B \pm b) = (A - B) \pm \sqrt{a^2 + b^2}$, where A,a and B,b are the means and standard deviations of the untreated and thiosulfate-treated samples, respectively.

[c] Measured as SRP-AA following UV-light photo-oxidation treatment (Armstrong et al., 1966).

ence of surface ocean (0–50 m) enrichments in SRP for 43% of our open-ocean profiles (Table 1). This unexpected surface ocean enrichment of SRP was reported by us in an earlier account of SRP distributions at Station ALOHA (Karl and Tien, 1992), and in a more comprehensive study by Haury et al. (1994). The latter study focused on nutrient distributions in the California Cooperative Oceanic Fisheries Investigations (CalCOFI) study region off southern California, but also presented data from several North Pacific Ocean transects. More than half of the 654 CalCOFI SRP profiles collected between 1950 and 1978 showed surface SRP enrichments. In addition, Haury et al. (1994) provided evidence for frequent near-surface enrichments of nitrate and silicate. The three nutrients (P, N and Si), however, did not systematically covary. Haury et al. (1994) concluded that:

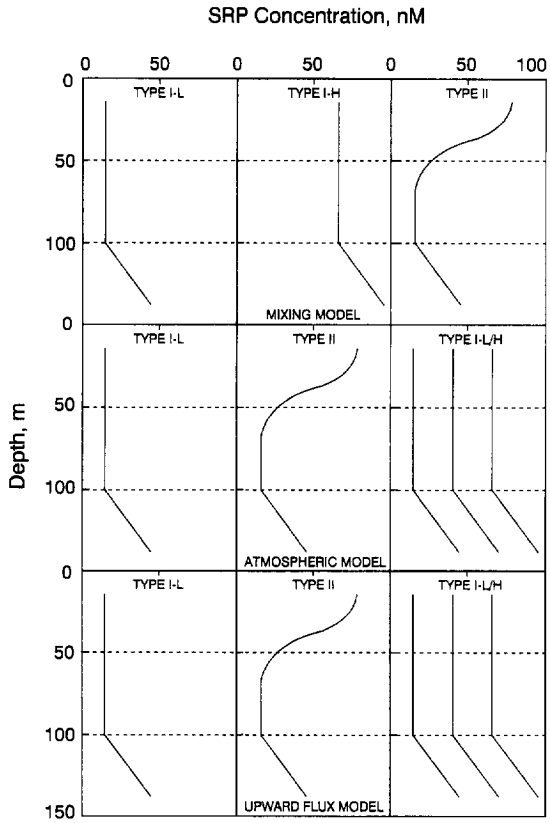


Fig. 10. Schematic representation of three independent but not mutually exclusive models to account for the variability in SRP-M concentrations in the near-surface waters at Station ALOHA: [TOP] mixing model, [CENTER] atmospheric deposition model and [BOTTOM] upward P flux model. In the mixing model, SRP is supplied from below the thermocline to produce a Type I-H profile, and subsequent net removal below the upper mixed-layer results in a Type-II SRP profile. In the atmospheric model, a Type I-L profile is transformed to a Type-II SRP profile by an episodic atmospheric P deposition event. Subsequent physical and biogeochemical dynamics of the upper water column could yield either Type I-L or H profiles, depending upon conditions. In the upward P flux model, P is transported to the near-surface waters either by active or passive transport mechanisms (see text), and depending upon physical and biogeochemical dynamics either a Type I-L or H could be produced.

> the frequency of occurrence of surface enrichment of a particular nutrient is inversely related to the complexity of the processes involved in the remineralization of that nutrient from its organic forms

At Station ALOHA, we also observe occasional near-surface enrichments in silica and nitrate. In the case of nitrate, our samples are routinely analyzed using both the chemiluminescence technique (Dore and Karl, 1996) and by standard autoanalyzer methods; the nitrate concentrations typically observed in the upper 100 m of the water column at Station ALOHA (5–15 nM) are well below the detection limit of the conventional autoanalyzer method. Similar to the results of Haury et al. (1994), the near-surface enrichments of SRP, nitrate and silica at Station ALOHA were independent.

In a previous report of *Trichodesmium* spp. blooms at Station ALOHA, Karl et al. (1992) presented two models to account for the observed accumulations of N_2-fixing microorganisms. Both explanations required a separation of upper water column N and P cycles, and both explicitly required an accumulation of P at the sea surface. We now expand these earlier discussions in light of the 6-yr data set on SRP and SNP distributions at Station ALOHA to three potential explanations. Although we present these models in schematic form as independent processes (Fig. 10), it is important to emphasize that they are not mutually exclusive.

In the simplest model (Fig. 10, top), deep mixing, especially during winter months, brings nutrients to the upper water column. This provides a mechanism to transform a Type I-L SRP profile into a Type I-H SRP profile within a period of < 1 week. Subsequent nutrient uptake by phytoplankton might be

expected to remove the imported nutrients restoring the initial system to a Type I-L SRP profile. However, differential rates of uptake, regeneration and export as a function of depth (i.e. light) could also produce a Type II SRP profile during a transition period. For example, the regeneration of SRP from DOP and particulate matter is most likely to be greatest at or near the surface where rates of primary production are greatest (Letelier et al., 1996). Furthermore, photochemical lysis could also be an important mechanism for SRP production from DOP. If a greater percentage of the nutrient incorporated at mid-euphotic zone depths was exported as sinking particulate matter, compared to surface waters, this could also produce a Type II SRP profile.

Deep mixing, however, would not necessarily provide a separation of N and P cycles or be expected to select for N_2-fixing microorganisms because both SRP and nitrate would be transported into the surface waters in a N/P ratio near to that of the elemental composition of plankton (i.e. 16 N : 1 P). Furthermore, it is difficult to invoke this mixing model to explain the frequent near-surface SRP accumulations during extended periods of calm weather (e.g., summer months). Consequently, this mechanism is incompatible with much of the Station ALOHA field data.

In the second model, the transition from a Type I-L to a Type II or Type I-H SRP profile is a result of the rapid atmospheric deposition of a relatively large concentration of phosphorus (i.e. > 1 mmol m^{-2} P in < 5 days). If the surface waters were well mixed (mixed-layer depth > 70 m), then an intermediate Type I SRP profile or Type I-H SRP profile would result, depending upon the total P flux. If the water column was stratified, a Type II SRP profile could result.

Atmospheric deposition of P has been measured at only a few sites in the North Pacific Ocean (Duce, 1986). These data suggest that P fallout is small, relative to the estimated upward eddy diffusive flux of P from below the euphotic zone. Furthermore, the N/P ratio of dry and wet deposition is generally greater than the N/P ratio in living organisms so atmospheric fallout should lead to coincident N and P enrichments and would not be expected to encourage the growth of N_2-fixing microorganisms. Finally, the atmospheric deposition processes studied to date derive from the highly seasonal Asian dust flux where deposition is greatest during late winter and early spring and almost non-existent during the rest of the year (Donaghay et al., 1991). Consequently, if this mechanism controlled SRP distributions in the upper water column at Station ALOHA we would observe Type II profiles only during late winter and early spring. This anticipated pattern is not only inconsistent with our data (Table 1), but it is also highly unlikely because of the generally deeper mixed-layers that are observed during this period of the year (Karl and Lukas, 1996).

In addition to the potential deposition of P associated with Asian dust, P derived from active volcanoes could provide an alternate source of P for selected regions of the world ocean. The volcanogenic P flux pathway relies upon the atmospheric deposition of soluble P into surface ocean waters and subsequent utilization by the resident microbial assemblages. Hawaiian volcanoes contain relatively high concentrations of P (up to 0.3% by weight as P_2O_5; Garcia et al., 1992) and are N poor, and could therefore comprise a mechanism for uncoupling surface ocean nutrient cycles at Station ALOHA especially during ENSO periods when the normal NE trade winds slacken and the volcanic plumes move northward towards our study area.

In laboratory experiments, Yamagata et al. (1991) demonstrated that P-containing rocks subjected to simulated magmatic conditions lose P_4O_{10} gas by volatilization. Upon rapid cooling, as might occur in the atmosphere, condensed phosphates including a large mole percentage of pyrophosphate (P_2O_7) are formed. Consequently, P extracted by volcanic activity on Hawaii could influence biogeochemical cycles at Station ALOHA. Field observations that are consistent with the predictions of this hypothesis include: (1) near-surface ocean SRP enrichments; (2) periodic pulses of SRP corresponding with periods of anomalous SE (i.e. "Kona") winds especially during ENSO (Karl et al., 1995); and (3) SRP pool changes that appear to be uncoupled from SNP pool fluctuations. All three conditions are observed at Station ALOHA.

There are at least two arguments against this model. First, arsenate, which is also known to be enriched in volcanic emissions does not co-vary with SRP as predicted by this model. However, it is

possible that the arsenic, which is concentrated in volcanic ash (Walsh et al., 1979) has a different impact zone from P; the latter is expected to be concentrated in the vapor phase. Second, this would not explain the existence of near-surface enrichments of SRP measured in regions far removed from active volcanoes (e.g., CalCOFI data set) or data from open-ocean stations north of Hawaii (Haury et al., 1994) collected prior to the present eruptive phase of Kilauea volcano which began in January 1983.

Alternatively, the third model postulates that the near-surface SRP enrichments arise from an accumulation of low-density organic matter (especially lipid-rich materials) at the air–water interface and subsequent release of SRP from enzymatic hydrolysis or in situ photolytic degradation (Fig. 10). Previous investigations in the North Pacific Ocean have documented the existence and quantitative significance of an "upward" particle flux (Simoneit et al., 1986; Smith et al., 1989). By definition, these materials are of lower density than seawater and are comprised largely of lipid, including phospholipids (Yayanos and Nevenzel, 1978). Under calm conditions, these materials could accumulate near the surface and produce a Type II SRP concentration profile. An important consequence of this model is that the upward flux of low-density particulate matter could provide the mechanism necessary to select for N_2-fixing microorganisms because the transport of materials with a low N/P ratio relative to that of living organisms would effect a separation of N and P cycles in the upper ocean.

In addition to this "passive" upward P flux mechanism discussed above, the possibility of active migrations of phytoplankton and zooplankton should also be considered. Karl et al. (1992) have previously suggested a "*Trichodesmium* shuttle" that relies to a large extent on unique physiological attributes of *Trichodesmium* to establish the N–P separation and P concentration prerequisites (Karl et al., 1992). A similar mechanism has also been suggested for the transport of nitrate in the North Pacific gyre by vertically migrating *Rhizosolenia* mats (Villareal et al., 1993).

In the *Trichodesmium* model, cells are required to sustain a periodic transfer of P from depths of 125–150 m to the ocean's surface. This is accomplished by intracellular P storage at depth, perhaps as volutin granules (Harold, 1966) under light-limited, P-saturated conditions. The energy required to sustain the cells during this P storage phase would be derived from excess carbohydrate previously accumulated during light-saturated growth in the near-surface waters. Either an external stimulus (e.g., decreased turbulence) or an internal stimulus (e.g., exhaustion of stored carbohydrate, accumulation of P) triggers the *Trichodesmium* population to form gas vacuoles providing a mechanism for the cells to change their position in the water column and, most importantly, increase their mean irradiance. Gas vacuolation and formation of carbohydrate are well-documented buoyancy and ballasting mechanisms, respectively, in *Trichodesmium* (Walsby, 1978; Kromkamp and Walsby, 1990; Villareal and Carpenter, 1990). Conditions near the sea surface are favorable for their growth because of high light, the ability to fix N_2 and stored polyphosphates. A surface enrichment would result partly from physical accumulation of cells and partly from net growth. When intracellular P is depleted, the cells continue to consume carbon that is stored as carbohydrate. Dinitrogen fixation in excess of anabolic requirements may also continue under these conditions, and could account for the observed increase in dissolved N throughout the ENSO period (Karl et al., 1995). Because the density of the storage carbohydrate is high relative to other cell constituents, the cells become negatively buoyant and sink to a position in the water column (perhaps determined by light, temperature or pressure) where active polyphosphate accumulation can again take place at the expense of stored carbohydrate catabolism. Given the published division rate estimates of natural populations (tens of days) and assuming the stored P can sustain 5–6 cell divisions, it is conceivable that there might exist a *Trichodesmium* cycle with a time scale of 100–150 days. This process of periodic migration is consistent with the 3–4-month "free-running cycle" of *Trichodesmium* that has been observed in the tropical Atlantic Ocean near Barbados (Steven and Glombitza, 1972) and may contribute to the near-surface SRP "pulses" observed in the Station ALOHA data set (Fig. 5). If active SRP scavenging occurs at mid-euphotic zone depths (i.e. 40–80 m) rather than at the base of euphotic zone, this process could also contribute to the formation of a Type II SRP concen-

tration vs. depth profile by a direct, rather than indirect, mechanism.

4. Conclusions

Our initial 6-yr investigation of biogeochemical processes at Station ALOHA has revealed an unexpectedly complex P cycle. The SRP pool dynamics are characterized by both high-frequency (months) and lower-frequency (6 yr) changes that may be related to larger-scale ocean–atmosphere interactions. Regardless of their cause, the dynamics of SRP, SNP and SRAs pools are likely to have an important influence on rates of total and export production and on the potential sequestration of atmospheric carbon dioxide during transient dissolved organic matter pool accumulation.

References

Anderson, L.C.D. and Bruland, K.W., 1991. Biogeochemistry of arsenic in natural waters: The importance of methylated species. Environ. Sci. Technol., 25: 420–427.

Andreae, M.O., 1978. Distribution and speciation of arsenic in natural waters and some marine algae. Deep-Sea Res., 25: 391–402.

Andreae, M.O., 1979. Arsenic speciation in seawater and interstitial waters: The influence of biological–chemical interactions on the chemistry of a trace element. Limnol. Oceanogr., 24: 440–452.

Armstrong, F.A.J., Williams, P.M. and Strickland, J.D.H., 1966. Photo-oxidation of organic matter in seawater by ultraviolet radiation, analytical and other applications. Nature (London), 211: 481–483.

Benson, A.A., 1984. Phytoplankton solved the arsenate–phosphate problem. In: O. Holm-Hansen, L. Bolis and R. Gilles (Editors), Marine Phytoplankton and Productivity. Lecture Notes in Coastal and Estuarine Studies, 8. Springer, Berlin, pp. 55–59.

Björkman, K. and Karl, D.M., 1994. Bioavailability of inorganic and organic phosphorus compounds to natural assemblages of microorganisms in Hawaiian coastal waters. Mar. Ecol. Prog. Ser., 111: 265–273.

Bossard, P. and Karl, D.M., 1986. The direct measurement of ATP and adenine nucleotide pool turnover in microorganisms: a new method for environmental assessment of metabolism, energy flux and phosphorus dynamics. J. Plankton Res., 8: 1–13.

Button, D.K., Dunker, S.S. and Morse, M.L., 1973. Continuous culture of *Rhodotorula rubra*: Kinetics of phosphate–arsenate uptake, inhibition, and phosphate-limited growth. J. Bacteriol., 113: 599–611.

Codispoti, L.A., 1989. Phosphorus vs. nitrogen limitation of new and export production. In: W.H. Berger, V.S. Smetacek and G. Wefer (Editors), Productivity of the Ocean: Present and Past. Wiley, New York, NY, pp. 377–394.

de Bettencourt, A.M.M., 1988. On arsenic speciation in the Tagus estuary. Neth. J. Sea Res., 22: 205–212.

Donaghay, P.L., Liss, P.S., Duce, R.A., Kester, D.R., Hanson, A.K., Villareal, T., Tindale, N.W. and Gifford, D.J., 1991. The role of episodic atmospheric nutrient inputs in the chemical and biological dynamics of oceanic ecosystems. Oceanography, 4: 62–70.

Dore, J.E. and Karl, D.M., 1996. Nitrite distributions and dynamics at Station ALOHA. Deep-Sea Res. II, 43: 385–402.

Dore, J.E., Houlihan, T., Hebel, D.V., Tien, G., Tupas, L. and Karl, D.M., 1996. Freezing as a method of sample preservation for the analysis of dissolved inorganic nutrients in seawater. Mar. Chem., 53: 173–185.

Downes, M.T., 1978. An automated determination of low reactive phosphorus concentrations in natural waters in the presence of arsenic, silicon and mercuric chloride. Water Res., 12: 743–745.

Duce, R.A., 1986. The impact of atmospheric nitrogen, phosphorus, and iron species on marine biological productivity, In: P. Buat-Menard (Editor), The Role of Air–Sea Exchange in Geochemical Cycling. D. Reidel, Boston, MA, pp. 497–529.

Fiske, C.H. and Subbarow, Y., 1925. The colorimetric determination of phosphorus. J. Biol. Chem., 66: 374–400.

Francesconi, K.A. and Edmonds, J.S., 1993. Arsenic in the sea. Oceanogr. Mar. Biol. Rev., 31: 111–151.

Garcia, M., Rhodes, J., Wolfe, E., Ulrich, G. and Ho, R., 1992. Petrology of lavas from episodes 2–47 of the Pu-u-o-o eruption of Kilauea volcano, Hawaii. Bull. Volcan., 55: 1–16.

Gordon, L.I., Jennings, Jr., J.C., Ross, A.A. and Krest, J.M., 1993. A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE hydrographic program and the Joint Global Ocean Fluxes Study. WOCE Hydrogr. Prog. Oper. Methods Manual, pp. 91–1.

Gorgy, S., Rakestraw, N.W. and Fox, D.L., 1948. Arsenic in the sea. J. Mar. Res., 7: 22–32.

Harold, F.M., 1966. Inorganic polyphosphates in biology: Structure, metabolism, and function. Bact. Rev., 30: 772–794.

Haury, L.R., Fey, C.L. and Shulenberger, E., 1994. Surface enrichment of inorganic nutrients in the North Pacific Ocean. Deep-Sea Res., 41: 1191–1205.

Johnson, D.L., 1971. Simultaneous determination of arsenate and phosphate in natural waters. Environ. Sci. Technol., 5: 411–414.

Johnson, D.L., 1972. Bacterial reduction of arsenate in sea water. Nature (London), 240: 44–45.

Johnson, D.L. and Burke, R.M., 1978. Biological mediation of chemical speciation, II. Arsenate reduction during marine phytoplankton blooms. Chemosphere, 7: 645–648.

Johnson, D.L. and Pilson, M.E.Q., 1972. Arsenate in the western North Atlantic and adjacent regions. J. Mar. Res., 30: 140–149.

Karl, D.M. and Lukas, R., 1996. The Hawaii Ocean Time-series (HOT) Program: Background, rationale and field implementation. Deep-Sea Res. II, 43: 129–156.

Karl, D.M. and Tien, G., 1992. MAGIC: A sensitive and precise method for measuring dissolved phosphorus in aquatic environments. Limnol. Oceanogr., 37: 105–116.

Karl, D.M. and Winn, C.D., 1991. A sea of change: Monitoring the oceans' carbon cycle. Environ. Sci. Technol., 25: 1976–1981.

Karl, D.M. and Yanagi, K., 1996. Partial characterization of the dissolved organic phosphorus pool in the oligotrophic North Pacific Ocean. Limnol. Oceanogr. (submitted).

Karl, D.M., Letelier, R., Hebel, D.V., Bird, D.F. and Winn, C.D., 1992. *Trichodesmium* blooms and new nitrogen in the North Pacific gyre. In: E.J. Carpenter, D.G. Capone and J.G. Rueter (Editors), Marine Pelagic Cyanobacteria: Trichodesmium and Other Diazotrophs. Kluwer, Dordrecht, pp. 219–237.

Karl, D.M., Tien, G., Dore, J. and Winn, C.D., 1993. Total dissolved nitrogen and phosphorus concentrations at US-JGOFS Station ALOHA: Redfield reconciliation. Mar. Chem., 41: 203–208.

Karl, D.M., Letelier, R., Hebel, D., Tupas, L., Dore, J., Christian, J. and Winn, C., 1995. Ecosystem changes in the North Pacific subtropical gyre attributed to the 1991–92 El Niño. Nature (London), 373: 230–234.

Karl, D.M., Christian, J.R., Dore, J.E., Hebel, D.V., Letelier, R.M., Tupas, L.M. and Winn, C.D., 1996. Seasonal and interannual variability in primary production and particle flux at Station ALOHA. Deep-Sea Res. II, 43: 539–568.

Kromkamp, J. and Walsby, A.E., 1990. A computer model of buoyancy and vertical migration in cyanobacteria. J. Plankton Res., 12: 161–183.

Letelier, R.M. and Karl, D.M., 1996. The role of *Trichodesmium* spp. in the productivity of the subtropical North Pacific Ocean. Mar. Ecol. Prog. Ser., 133: 263–273.

Letelier, R.M., Bidigare, R.R., Hebel, D.V., Ondrusek, M., Winn, C.D. and Karl, D.M., 1993. Temporal variability of phytoplankton community structure based on pigment analysis. Limnol. Oceanogr., 38: 1420–1437.

Letelier, R.M., Dore, J.E., Winn, C.D. and Karl, D.M., 1996. Seasonal and interannual variations in photosynthetic carbon assimilation at Station ALOHA. Deep-Sea Res. II, 43: 467–490.

Murphy, J. and Riley, J.P., 1962. A modified single solution method for determination of phosphate in natural waters. Anal. Chim. Acta, 27: 31–36.

Orrett, K. and Karl, D., 1987. Dissolved organic phosphorus production and turnover in surface waters. Limnol. Oceanogr., 32: 383–395.

Redfield, A.C., Ketchum, B.H. and Richards, F.A., 1963. The influence of organisms on the composition of plankton. In: M.N. Hill (Editor), The Sea, Ideas and Observations on Progress in the Study of the Seas, Vol. 2. Interscience, New York, NY, pp. 26–77.

Ridal, J.J. and Moore, R.M., 1990. A re-examination of the measurement of dissolved organic phosphorus in seawater. Mar. Chem., 29: 19–31.

Simoneit, B.R.T., Grimalt, J.O., Fischer, K. and Dymond, J., 1986. Upward and downward flux of particulate organic material in abyssal waters of the Pacific Ocean. Naturwissenschaften, 73: 322–325.

Smith, Jr., K.L., Williams, P.M. and Druffel, E.R.M., 1989. Upward fluxes of particulate organic matter in the deep North Pacific. Nature (London), 337: 724–726.

Solorzano, L. and Strickland, J.D.H., 1968. Polyphosphate in seawater. Limnol. Oceanogr., 13: 515–518.

Steven, D.M. and Glombitza, R., 1972. Oscillatory variation of a phytoplankton population in a tropical ocean. Nature (London), 237: 105–107.

Strickland, J.D. and Parsons, T.R., 1965. A Manual of Seawater Analysis. Fish. Res. Board Can. Bull., 1st ed.

Strickland, J.D. and Parsons, T.R., 1972. A Practical Handbook of Seawater Analysis. Fish. Res. Board Can., Bull. No. 167, 2nd ed.

Villareal, T.A. and Carpenter, E.J., 1990. Diel buoyancy regulation in the marine diazotrophic cyanobacterium *Trichodesmium thiebautii*. Limnol. Oceanogr., 35: 1832–1837.

Villareal, T.A., Altabet, M.A. and Culver-Rymsza, K., 1993. Nitrogen transport by vertically migrating diatom mats in the North Pacific Ocean. Nature (London), 363: 709–712.

von Schouwenburg, J.C. and Walinga, I., 1967. The rapid determination of phosphorus in the presence of arsenic, silicon and germanium. Anal. Chim. Acta, 37: 269–271.

Walsby, A.E., 1978. The properties and buoyancy-providing role of gas vacuoles in *Trichodesmium* Ehrenberg. Br. Phycol. J., 13: 103–116.

Walsh, P.R., Duce, R.A. and Fasching, J.L., 1979. Considerations of the enrichment, sources, and flux of arsenic in the troposphere. J. Geophys. Res., 84: 1719–1726.

Winn, C.D., Mackenzie, F.T., Carrillo, C.J., Sabine, C.L. and Karl, D.M., 1994. Air–sea carbon dioxide exchange in the North Pacific subtropical gyre: Implications for the global carbon budget. Global Biogeochem. Cycles, 8: 157–163.

Yamagata, Y., Watanabe, H., Saitoh, M. and Namba, T., 1991. Volcanic production of polyphosphates and its relevance to prebiotic evolution. Nature (London), 352: 516–519.

Yayanos, A.A. and Nevenzel, J.C., 1978. Rising-particle hypothesis: Rapid ascent of matter from the deep ocean. Naturwissenschaften, 65: 255–256.