

Distributions of particulate and dissolved organic and inorganic phosphorus in North Pacific surface waters

Takeshi Yoshimura^{a,*}, Jun Nishioka^b, Hiroaki Saito^c, Shigenobu Takeda^d,
Atsushi Tsuda^e, Mark L. Wells^f

^a Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko, Chiba 270-1194, Japan

^b Institute of Low Temperature Science, Hokkaido University, Sapporo, 060-0819, Japan

^c Tohoku National Fisheries Research Institute, Fisheries Research Agency, Shiogama, Miyagi 985-0001, Japan

^d Department of Aquatic Bioscience, Faculty of Agriculture, The University of Tokyo, Bunkyo, Tokyo 113-8657, Japan

^e Ocean Research Institute, The University of Tokyo, Nakano, Tokyo 164-8639, Japan

^f School of Marine Sciences, University of Maine, Orono, ME 04469-5741, USA

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Abstract

Several operationally defined fractions of phosphorus (P) were measured along a surface water transect in the North Pacific. The P content in all fractions was found to increase northward from the edge of the subtropical to the subarctic region. Particulate organic P (POP) concentrations increased from 9 to 110 nmol L⁻¹, whereas the particulate inorganic P (PIP) concentrations increased from 1 to 13 nmol L⁻¹. A significant correlation between POP, PIP and chlorophyll *a* suggested that these P pools are associated directly or indirectly with phytoplankton cells. PIP comprised 10–20% of the total particulate P pool across the transect, indicating it is an important component of the marine P cycle in this region. Dissolved non-reactive P (assumed to consist predominantly of non-reactive organic P compounds, thus referred to as DOP) concentration increased from 0.10 to 0.22 μmol L⁻¹, whereas soluble reactive P (SRP) concentration increased from 0.01 to 1.42 μmol L⁻¹ along the transect. The proportion of DOP and SRP varied widely, with a large proportion of DOP in areas with low total dissolved P concentrations in lower latitudes and a large proportion of SRP in areas with high total dissolved P concentrations in higher latitudes. High demand for DOP in the lower latitudinal region would diminish the concentration of this pool relative to higher latitudinal regions where SRP is more abundant and would be preferentially utilized. The availability of SRP could have a significant impact on the concentration and probably on the composition of DOP. We show that P fractionation provides an important insight for discussing the marine P cycle.

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1. Introduction

Phosphorus (P) is an essential element for all living organisms. It plays important roles in living cells as a

constituent of genetic materials (e.g., DNA, RNA) as well as energy-producing (e.g., ATP) and cellular (e.g., phospholipids) compounds. Phosphorus concentrations generally are low in seawater and can limit biological productivity in some marine ecosystems (Thingstad et al., 1998; Karl et al., 2001). Even so, studies concerning the P cycle are relatively sparse in comparison to the more

* Corresponding author. Tel.: +81 47182 1181; fax: +81 47183 2966.

E-mail address: ytakeshi@criepi.denken.or.jp (T. Yoshimura).

comprehensive study of carbon (C) and nitrogen (N) dynamics in the ocean. Given that the marine P cycle is closely linked to that of C and N, better characterization of P cycling will improve our understanding of marine biogeochemistry and its relationship to plankton dynamics. Moreover, better insights to these linkages are essential for more accurately predicting climate change effects on marine ecosystems.

Phosphorus in seawater exists in both particulate and dissolved pools, each of which contain organic and inorganic forms. Total dissolved P (TDP) usually is defined as that fraction passing through 0.1–1 μm pore-sized filters and is partitioned into dissolved inorganic P (DIP) and dissolved organic P (DOP). The DIP pool consists of orthophosphate, pyrophosphate and polyphosphate, whereas DOP, which can comprise a major fraction of dissolved P, has not been fully characterized (Karl and Björkman, 2002). Total particulate P (TPP) also exists in inorganic P (PIP) and organic P (POP) forms. Particulate inorganic occurs in mineral phases, adsorbed to particles (biotic and abiotic) and as intracellular storage products (orthophosphate, pyrophosphate and polyphosphate), whereas POP comprises P incorporated in living and detrital organic molecules. Because these different fractions vary in their bioavailability and turnover times, information about the size and dynamics of each pool is necessary to characterize the P cycle.

Chemical fractionation methods do not necessarily correspond to these conceptual P pools (DIP, DOP, PIP and POP), and distinguishing among these pools by chemical analysis is operationally defined. Orthophosphate in the TDP pool has traditionally been measured by

the molybdenum blue colorimetric method (Murphy and Riley, 1962). However, a fraction of inorganic condensed phosphates (pyrophosphate and polyphosphate) and acid-labile organic P can be hydrolyzed to orthophosphate during this analysis (Thomson-Bulldis and Karl, 1998). For this reason, P measured with the current molybdenum blue method is termed soluble reactive P (SRP) (Strickland and Parsons, 1972). The TDP pool thus is partitioned into SRP and soluble non-reactive P (SNP, TDP minus SRP). Because orthophosphates usually comprise a major portion of DIP concentrations in the open ocean (Solórzano and Strickland, 1968), SRP is roughly equivalent to DIP in these waters. In contrast, SNP contains not only DOP but also inorganic condensed phosphates. However, because the latter concentrations are very low in the open ocean (Solórzano and Strickland, 1968), SNP often is considered roughly equivalent to DOP. More sophisticated chemical fractionation methods, including sequential extraction, and nuclear magnetic resonance (NMR) analyses have been used to fractionate TPP in sediment and sinking particulates into PIP and POP (Ruttenberg, 1992; Paytan et al., 2003; Faul et al., 2005), but these methods require relatively large sample sizes. To avoid this requirement, a straightforward acid extraction method has been developed to divide the TPP pool into PIP and POP (TPP minus PIP) (Loh and Bauer, 2000; Benitez-Nelson et al., 2004). While intercomparison between these methods still is needed, the acid extraction approach is especially useful in open ocean waters where it is difficult to obtain large amounts of particulate matter.

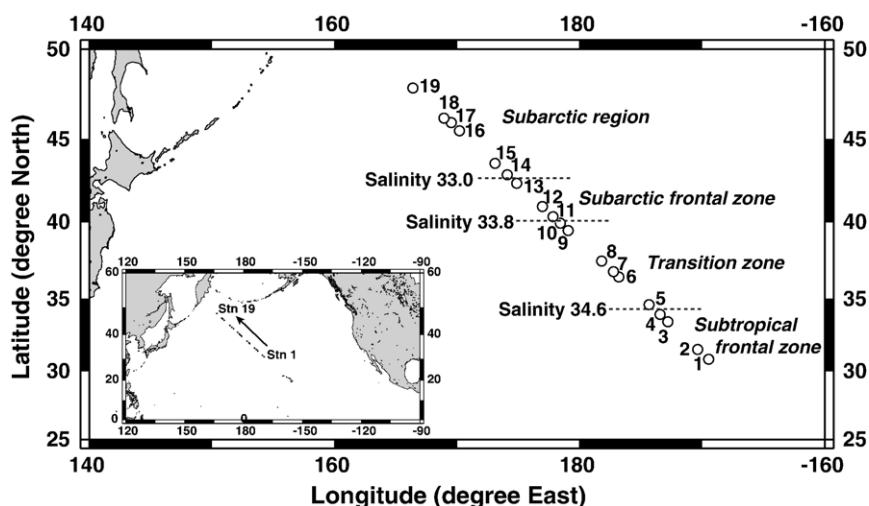


Fig. 1. Locations of sampling stations 1–19 along a transect cruise on July 2004, showing approximate section of the ocean regions with reference salinity as described in Roden (1991) (see detail in Section 3.1). Figure reproduced using Online Map Creation (<http://www.aquarius.geomar.de/omc/>).

Table 1

Sample description, seawater temperature, salinity, chlorophyll *a* (Chl *a*), total particulate phosphorus (TPP) and total dissolved phosphorus (TDP) concentrations in each underway sampling stations along a transect in the North Pacific

Station no.	Latitude (°N)	Longitude	Local time		Temp. (°C)	Sal.	Chl <i>a</i> (µg L ⁻¹)	TPP (nmol L ⁻¹)	TDP (µmol L ⁻¹)
1	30.8	169.5°E	19-July-2004	13:15	24.97	35.00	0.08	ND	0.12
2	31.5	170.4°E	19-July-2004	20:17	25.51	35.05	0.09	14	0.11
3	33.4	172.8°E	20-July-2004	8:33	24.77	34.77	0.09	13	0.14
4	33.9	173.4°E	20-July-2004	13:11	25.01	34.74	0.08	12	0.15
5	34.6	174.3°E	20-July-2004	20:12	24.64	34.36	0.08	20	0.20
6	36.5	176.8°E	21-July-2004	9:58	23.32	34.48	0.13	20	0.22
7	36.8	177.2°E	21-July-2004	13:15	23.03	34.45	0.12	21	0.21
8	37.5	178.2°E	21-July-2004	19:32	23.33	34.33	0.13	26	0.21
9	39.5	179.1°W	23-July-2004	8:00	20.61	33.92	0.39	60	0.26
10	39.9	178.4°W	23-July-2004	13:17	19.58	33.82	0.40	65	0.33
11	40.3	177.8°W	23-July-2004	17:18	17.20	33.43	0.61	66	0.62
12	41.0	177.0°W	23-July-2004	22:02	18.83	34.27	0.20	43	0.19
13	42.4	174.9°W	24-July-2004	8:28	15.87	33.81	0.84	105	0.31
14	42.9	174.1°W	24-July-2004	13:11	12.83	32.94	0.54	66	1.20
15	43.6	173.1°W	24-July-2004	19:42	12.01	33.00	0.57	69	1.19
16	45.5	170.2°W	25-July-2004	8:47	9.40	32.82	0.62	82	1.49
17	46.0	169.5°W	25-July-2004	13:14	8.93	32.82	0.37	59	1.55
18	46.2	168.9°W	25-July-2004	18:11	9.16	32.82	0.37	61	1.53
19	47.9	166.4°W	26-July-2004	6:31	8.58	32.88	1.35	123	1.64

ND: no data available.

Although there now exists a large dataset for SRP in the world oceans (e.g., Conkright et al., 2000), concentrations of other forms of P have scarcely been measured, and this is particularly true for the particulate phase. Given that exchange among these various pools regulates P cycling, better characterization of the spatial and temporal distributions of these various forms of P is needed to improve our understanding of P biogeochemistry.

In this study, we measured the operationally defined organic and inorganic forms of particulate and dissolved P along a transect through the oligotrophic subtropical and nutrient-rich subarctic regions of the North Pacific. These results provide new insights into the spatial differences in the various P pools and their apparent linkages to the physical and biological environments of each region.

2. Materials and methods

The study was conducted during the R/V Kilo Moana cruise KM0415. Seawater samples were collected from ~6 m depth using the vessel's underway pumping system at 19 stations from 19 July 2004 to 26 July 2004 (Fig. 1 and Table 1). Each sample was homogenized in an acid-cleaned 9-L polycarbonate carboy equipped with a spigot (Nalgene) and subsampled for particulate and dissolved P, and chlorophyll *a* (Chl *a*) analyses. Subsamples were drawn for dissolved P by gravity-filtration through an in-line capsule cartridge filter (0.20 µm pore size polyethersulfone membrane and polypropylene housing,

Advantec). Filtered subsamples were collected in amber glass bottles, sealed with Teflon-lined caps and stored at -20 °C until analysis. Subsamples were filtered through duplicate filters for particulate P analysis, one for TPP and one for PIP. One 2-L aliquots of seawater were filtered through a precombusted (450 °C for 4 h) and acid-washed (1 N HCl) Whatman GF/F filter under vacuum at <0.01 MPa. These filters were stored at -20 °C until analysis back in the on-shore laboratory. For Chl *a* analysis, 126 mL subsamples were filtered (Whatman GF/F) under vacuum at <0.01 MPa, and the filters extracted with *N,N*-dimethylformamide at -20 °C in the dark for ~24 h (Suzuki and Ishimaru, 1990). Chlorophyll *a* concentrations were measured onboard by fluorometry (Turner Designs Model 10-AU) as described in Welschmeyer (1994). Seawater temperature and salinity were measured with a shipboard thermosalinograph (Sea-Bird, SBE21) situated in the seawater intake line.

Soluble reactive P was measured by the molybdenum blue method (Hansen and Koroleff, 1999). Samples for TDP analysis were autoclaved in an acid potassium persulfate solution at 123 °C for 120 min (Ridal and Moore, 1990; Hansen and Koroleff, 1999). Total dissolved P concentrations were measured as SRP after removing excess free chlorine by placing the samples in a hot water bath for 2 h. The detection limit, given as three times the standard deviation of 10 blank measurements, for SRP and TDP was 0.01 µmol L⁻¹. Analyses for SRP and TDP were done on a single sample that was

analyzed in duplicate and mean value was reported. The SNP concentrations were calculated by difference between TDP and SRP and these are assumed here to correspond to DOP. Taking into account error propagation, the precision of the SNP concentrations was $\pm 0.04 \mu\text{mol L}^{-1}$. Total particulate P was measured after high temperature combustion and acid hydrolysis of the filters as described by Solórzano and Sharp (1980). Particulate inorganic P was extracted from filter samples with 1 N HCl at 20 °C in the dark for 24 h and quantified as SRP (Aspila et al., 1976). Analyses for TPP and PIP were done on a single sample that was analyzed in duplicate and mean value was reported. Particulate organic P concentrations were calculated as the difference between TPP and PIP. A higher precision ($< \pm 1 \text{ nmol L}^{-1}$) was obtained for particulate P analyses

due to the ca. 30-fold concentration factor used in the analytical procedure.

To confirm that sampling artifacts were not introduced to the underway sampling stream (e.g., physical stress associated with the shipboard pump or the activity of attached microbial communities), comparisons were made between surface samples collected with a Niskin bottle and the underway pumping system at 6 stations of the 19 stations (stations 1, 4, 7, 10, 14 and 17). Sample pairs were analyzed for Chl *a*, SRP and DOP concentrations, and the differences between these ranged from 0.00 to 0.04 $\mu\text{g L}^{-1}$ for Chl *a*, 0.01 to 0.02 $\mu\text{mol L}^{-1}$ for SRP and 0.00 to 0.02 $\mu\text{mol L}^{-1}$ for DOP. These ranges are within the limits of analytical error, indicating that the underway samples indeed are representative of the natural conditions.

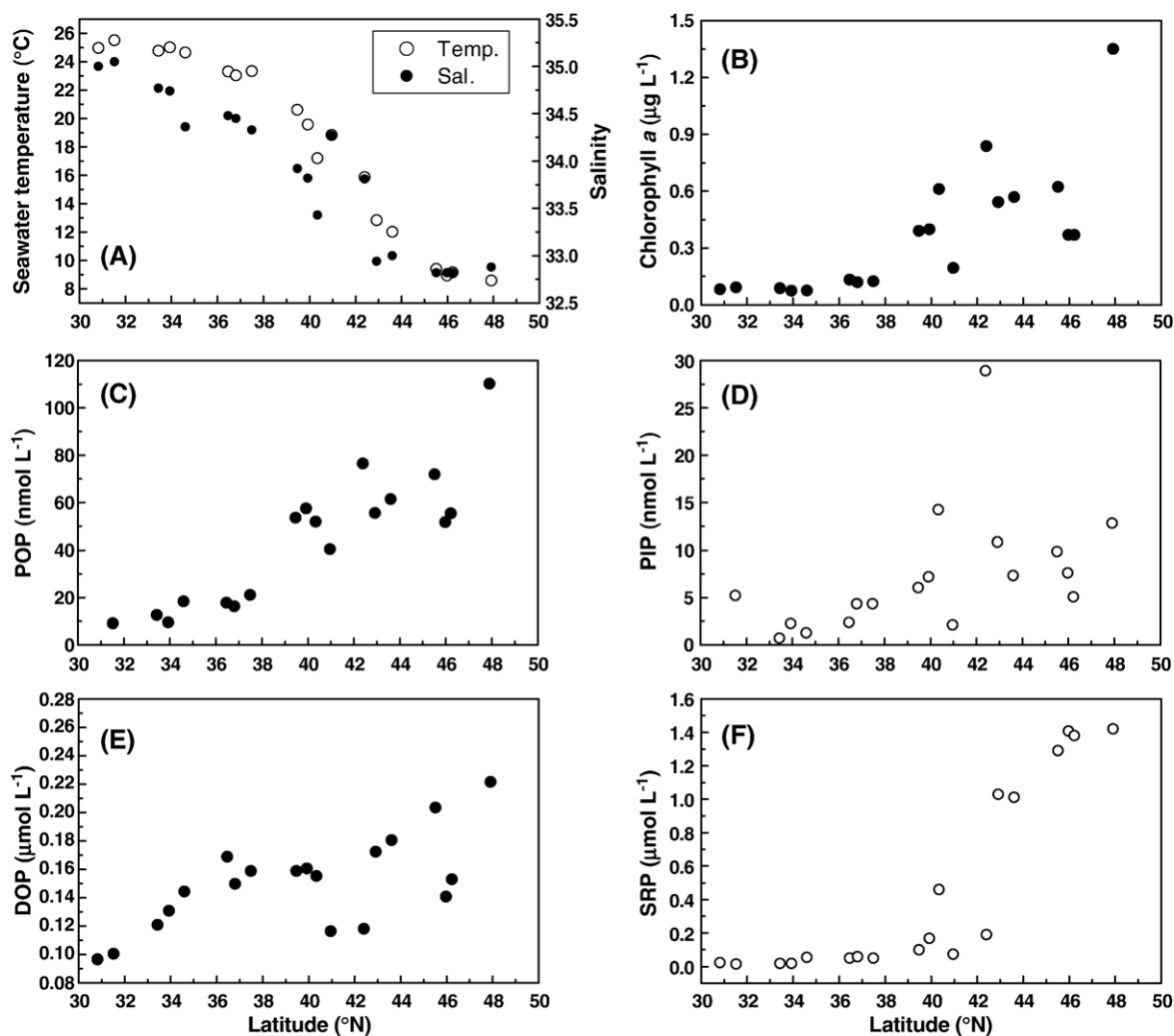


Fig. 2. Latitudinal variations in (A) seawater temperature and salinity, (B) chlorophyll *a*, (C) particulate organic phosphorus (POP), (D) particulate inorganic phosphorus (PIP), (E) dissolved organic phosphorus (DOP) and (F) soluble reactive phosphorus (SRP).

3. Results and discussion

3.1. Physical and biological environments

The sampling stations were located from the edge of the subtropical to the subarctic region and thus the seawater samples spanned a wide range of physical and biological environments. Seawater temperatures decreased from 25.5 °C to 8.6 °C from station 1 through station 19 and salinity decreased from 35.1 to 32.8 (Fig. 2A, Table 1). Chlorophyll *a* concentrations remained constant at $\sim 0.1 \mu\text{g L}^{-1}$ from station 1 through station 8, but increased further northward up to $1.35 \mu\text{g L}^{-1}$ (Fig. 2B, Table 1). According to the latitude and salinity indices of Roden (1991), stations 1–4 were situated in the subtropical frontal zone, stations 5–10 in the subarctic–subtropical transition zone, stations 11–13 in the subarctic frontal zone and

stations 14–19 in the subarctic region. However, these classifications are imperfect; seawater temperature and salinity at stations 12 and 13 had water mass characteristics of the transition zone water (Fig. 2A). On the other hand, Chl *a* concentrations were within the typical range for each region (Odate and Maita, 1988/1989). Samples across this transect were characterized by phytoplankton assemblages of different sizes and composition. Chlorophyll *a* mainly is attributed to small-sized phytoplankton ($< 2 \mu\text{m}$) from the subtropical region to the subarctic region when the concentration is less than $1 \mu\text{g L}^{-1}$ (Odate and Maita, 1988/1989). A measurement of the chemotaxonomic pigments elucidated that *Prochlorococcus* account for about half of the Chl *a* biomass around the subtropical frontal zone (Suzuki et al., 1995). In the transition zone, prymnesiophytes and *Synechococcus* dominate the phytoplankton population (Ishizaka et al., 1994; Suzuki et al., 1997),

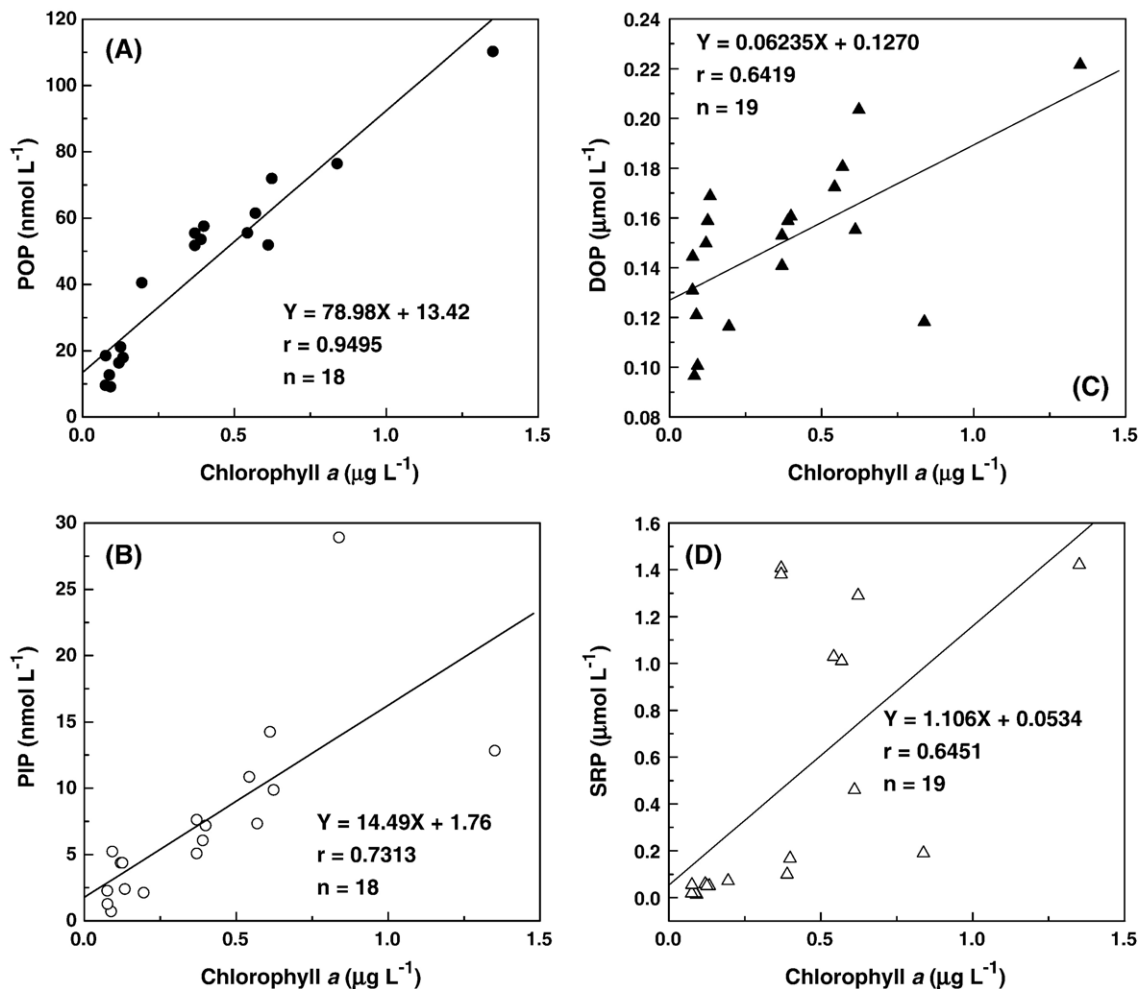


Fig. 3. Correlations between (A) particulate organic phosphorus (POP), (B) particulate inorganic phosphorus (PIP), (C) dissolved organic phosphorus (DOP) and (D) soluble reactive phosphorus (SRP) and chlorophyll *a*.

whereas prasinophytes and diatoms dominate the phytoplankton population in the subarctic region (Obayashi et al., 2001; Suzuki et al., 2002). Large-sized Chl *a* (>10 μm), predominantly of diatoms, dominate in the region where Chl *a* concentrations exceed $1 \mu\text{g L}^{-1}$ (Odate and Maita, 1988/1989), as seen at our station 19 ($1.35 \mu\text{g Chl } a \text{ L}^{-1}$).

3.2. Particulate phosphorus pools

Total particulate P concentrations increased northward, ranging from 12 to 123 nmol L^{-1} (Table 1). Particulate organic P concentrations increased from 9 nmol L^{-1} (station 2) to 110 nmol L^{-1} (station 19) (Fig. 2C), whereas PIP concentrations increased from 1 to 13 nmol L^{-1} across the same transect, with an exceptionally high value of 29 nmol L^{-1} at station 13 (Fig. 2D). The POP concentrations correlated closely with Chl *a* concentrations ($r=0.950$, $n=18$; Fig. 3A). While this correlation may not be causative, it may suggest that the POP pool was composed of mainly living algal cell constituents, including nucleic acids, nucleotides and phospholipids (Paytan et al., 2003). Previous reports also have suggested that particulate organic matter reflects phytoplanktonic

cellular constituents and to a lesser extent that of bacteria and zooplankton (Copin-Montegut and Copin-Montegut, 1983). On the other hand, PIP comprised 5–36% of the TPP pool along the transect, with typical range of 10–20% (Fig. 4A) and this fraction also showed a significant positive correlation with Chl *a* concentrations ($r=0.731$, $n=18$; Fig. 3B). This finding is not particularly surprising given that, in addition to P incorporated within mineral phases, the acid extractable particulate P pool would include labile organic matter (hydrolyzed with 1 N HCl), P adsorbed onto biotic (or abiotic) particles as well as intracellular P stores, in which pyrophosphate and polyphosphate may not have been fully hydrolyzed in 1 N HCl at $20 \text{ }^\circ\text{C}$ (Solórzano and Strickland, 1968). Given that supplies of terrigenous materials through riverine or aerial transport would be very small in this open ocean region, mineral contributions to PIP likely were minor. Furthermore, in fresh marine organic matter, only a very small percentage of the POP is hydrolyzed by 1 N HCl (Ingall and Cappellen, 1990). The significant correlation of PIP and Chl *a* indicates that P is associated with living bio-particles, and especially phytoplankton. Intracellular phosphate has been found to be large fraction of phytoplanktonic TPP (Miyata and Hattori, 1986; Paytan et al., 2003) and plankton surface-adsorbed P also is reported to be an important source of PIP (Sañudo-Wilhelmy et al., 2004; Fu et al., 2005).

These data add further support to findings that PIP can be an important constituent of the marine particulate P pool. Although particulate P traditionally was assumed to represent primarily POP, this assumption has been critically tested only recently by studies that measured both POP and PIP. Loh and Bauer (2000) adopted an acid extraction method to divide the TPP pool into POP and PIP. They reported values of surface water POP concentrations of $10.5\text{--}37.3 \text{ nmol L}^{-1}$ in the eastern North Pacific and 13.5 nmol L^{-1} in the Southern Ocean, which are consistent with our results for the subtropical frontal zone and the transition zone. Particulate organic P concentrations in the subarctic region in our study were substantially higher, which we attribute to the higher phytoplankton biomass. On the other hand, surface PIP concentrations along our transect were lower than their reported values of $12.7\text{--}18.9 \text{ nmol L}^{-1}$ in the eastern North Pacific and 27.6 nmol L^{-1} in the Southern Ocean (Loh and Bauer, 2000). In their case, PIP accounted for 26–67% of TPP in those regions (Loh and Bauer, 2000); i.e., higher than the 5–36% we observed. Paytan et al. (2003) also showed a relatively higher proportion of PIP than our results by using NMR analyses. In their study, TPP in a $75 \mu\text{m}$ plankton tow sample composed mainly of diatoms was 53% POP and

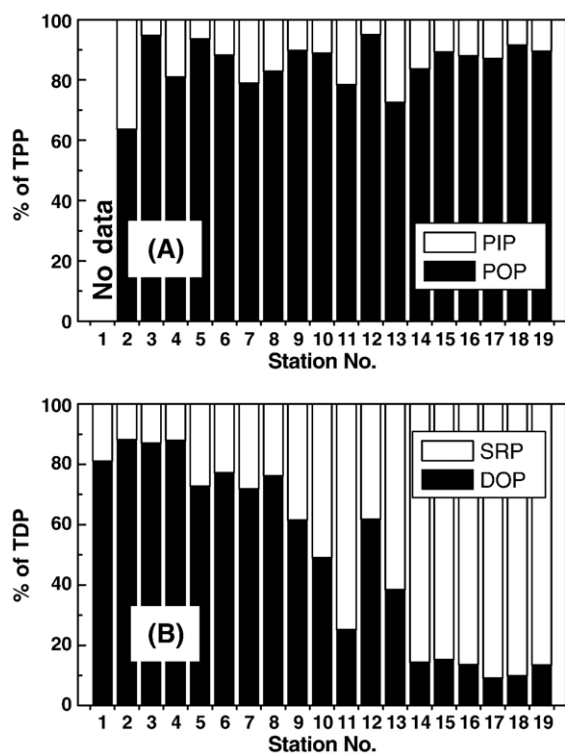


Fig. 4. Proportions of (A) particulate organic phosphorus (POP) and particulate inorganic phosphorus (PIP) in total particulate phosphorus (TPP), (B) dissolved organic phosphorus (DOP) and phosphorus (SRP) in total dissolved phosphorus (TDP).

47% PIP (Paytan et al., 2003). Potential factors that might explain these differences are variations in planktonic species composition, the physiological status of phytoplankton (Sañudo-Wilhelmy et al., 2004), the physical and chemical quality of the particles, or methodological differences. Even so, our results support the findings of these studies that PIP comprises a significant proportion of TPP in the ocean. Similarly, Loh and Bauer (2000) reported that the PIP accounted for approximately 60% of the TPP sinking flux. Recent sediment trap studies also have elucidated that PIP comprises a large proportion of TPP in sinking particles (Paytan et al., 2003; Benitez-Nelson et al., 2004; Faul et al., 2005). Paytan et al. (2003) showed that 45–65% of NaOH–EDTA extractable P from the sinking particulate matter was found to be inorganic P (predominantly orthophosphate) in the majority of regions and depths. Using an acid extraction method, Benitez-Nelson et al. (2004) report that PIP comprises 39–88% of TPP flux in the upper trap (275 m) in the Cariaco Basin. Using a sequential extraction method, Faul et al. (2005) report that a large proportion of sinking P occurs in the authigenic, oxide associated, labile and detrital P pools, which would correspond largely to our acid-extracted PIP fraction. Thus, both P distribution and P flux studies demonstrate that PIP has an important role in the marine P cycle.

Recognizing that PIP comprises a significant portion of TPP has implications for use of the elemental stoichiometry of particulate matter. An inherent assumption when considering the Redfield ratio of 106C/16N/1P for authigenic marine particulate matter (Redfield et al., 1963) is that particulate P=POP (e.g., Kolowitz et al., 2001). Based on the findings here and in earlier studies (e.g., Faul et al., 2005), this assumption will overestimate P related to organic matter unless there is careful distinction between PIP and POP. By the detailed TPP characterization using sequential extraction method, Faul et al. (2005) suggest that not only acid-insoluble TPP (i.e., POP) but also very labile organic P and authigenic P components, which are not included in the acid-insoluble POP pool, must be included in P fraction when the degree of preferential regeneration of P relative to C is discussed about sinking organic matter. It may not be the case for suspended particles in surface waters because the chemical nature of P in suspended particles is likely to be different from that of sinking particles; for example, the proportion of acid-insoluble POP in the TPP pool is higher in suspended particles in surface water (80–90% in this study) than ~40% values in sinking particles (Faul et al., 2005). Better characterization of acid extractable PIP and acid-insoluble POP in the marine particulate phase is needed to explore this issue. Certainly, the findings here (Fig. 4A) suggest that PIP needs to be taken more into

account when considering POM stoichiometry over a wide range of marine environments.

Although the procedure used in this study to quantify PIP vs. POP is simplistic compared to the more refined, time consuming procedures used by Miyata and Hattori (1986), Ruttenberg (1992) and Faul et al. (2005), it still provides meaningful insights. An intercomparison of the simple acid extraction method with more complex characterization methods of TPP analysis is needed to enable these datasets to be compared. Even so, expanding the use of the acid extraction for TPP analysis to other oceanographic regions and temporal scales will greatly improve our understanding of the biogeochemical cycling of P.

3.3. Dissolved phosphorus pools

Total dissolved P concentrations increased northward along with TPP concentrations, from 0.11 to 1.64 $\mu\text{mol TDP L}^{-1}$ (Table 1). Dissolved organic P concentrations doubled from 0.10 to 0.22 $\mu\text{mol L}^{-1}$ along this transect (Fig. 2E), whereas SRP concentrations increased by two orders of magnitude from 0.01 to 1.42 $\mu\text{mol L}^{-1}$ (Fig. 2F). The increase in DOP concentration was gradual and values remained constant across the transition zone (stations 5 to 10). Soluble reactive P concentrations on the other hand remained less than 0.06 $\mu\text{mol L}^{-1}$ at stations 1–8 but increased rapidly up to 1.42 $\mu\text{mol L}^{-1}$ at station 19. Although the correlations of DOP and SRP with Chl *a* were statistically significant at a 95% confidence limit, their correlation coefficients were much lower than that between particulate P forms and Chl *a* (Fig. 3C,D). This result suggests that P alone is not necessarily the limiting nutrient for phytoplankton biomass throughout the regions in the North Pacific. While P limitation is prevalent in the subtropical gyre (near station 1) (Karl et al., 2001), single or combination of P, N, iron (Fe) and zooplankton grazing potentially limit phytoplankton biomass in other regions. Recently, in the subarctic North Pacific (near station 19), in-situ Fe enrichment experiments elucidates that phytoplankton growth is limited by Fe (Tsuda et al., 2003). While SRP made up only 12–19% of the TDP pool in the subtropical frontal zone (stations 1–4), this proportion increased across the transition zone (stations 5–10) and the subarctic frontal zone (stations 11–13), to 85–91% in the subarctic region (stations 14–19) (Fig. 4B). Due in part to the very low SRP in the subtropical frontal zone, DOP is considered to be an important P source for phytoplankton and bacteria (Björkman and Karl, 2003). High demand for DOP in the subtropical frontal zone is likely to be one of reasons to diminish the concentration of this pool relative

to higher latitudinal regions where SRP is more abundant and would be preferentially utilized. Indeed, the SRP concentration was high in the subarctic region due to the upwelling of the SRP rich deep water and the low demand for DOP maintains relatively high DOP concentrations. Availability of SRP for phytoplankton and bacteria would thus have an impact on the DOP pool size and probably on the composition of DOP as well.

There are few studies on the spatial distribution of DOP in surface waters. Abell et al. (2000) measured total organic P (TOP; TPP plus DOP concentration using the same definitions as in our study) along a north–south transect between 10°N and 45°N in the eastern North Pacific. They showed that surface TOP concentrations decreased from 0.35 $\mu\text{mol L}^{-1}$ at 14°N to 0.10 $\mu\text{mol L}^{-1}$ at 35°N and then increased to $\sim 0.2 \mu\text{mol L}^{-1}$ at the northern margin of the transect. In the North Pacific, the majority of TOP existed in dissolved forms (Fig. 2 and Table 1 in this study; Karl et al., 2001) and the trend in TOP concentrations from the subtropical frontal zone to the subarctic frontal zone reported in Abell et al. (2000) was similar to the DOP concentrations reported here (0.10–0.22 $\mu\text{mol L}^{-1}$). There was a distinct minimum in DOP (and TOP) concentrations in the subtropical frontal zone in both our results and those of Abell et al. (2000), suggesting that this pattern may be a general feature in the North Pacific. The reason for this apparent geographical minimum is not known and awaits further study, but presumably will be linked to some combination of autochthonous and allochthonous supply rates of SRP and DOP, the relative lability of DOP produced in this region, bioavailability of Fe, phytoplankton species composition, microbial activity or the rates of N_2 fixation.

Some of the more comprehensive studies of marine P dynamics have been conducted at the Hawaii Ocean Time-series (HOT) site (Station ALOHA, 22.75°N, 158°W) in the North Pacific subtropical gyre. Here DOP concentrations ranged from 0.15–0.30 $\mu\text{mol L}^{-1}$ with a mean of 0.23 $\mu\text{mol L}^{-1}$ in the upper 100 m of the water column between 1988 and 1997 (Karl et al., 2001). These DOP concentrations at Station ALOHA are generally higher than we found in the subtropical frontal zone, but, as noted above, this difference is consistent with previous reports of higher DOP concentrations in the region south of our sampling area (Abell et al., 2000). In contrast, Vidal et al. (1999) reported DOP concentrations along a transect from 26°N to 36°S in the central Atlantic and found DOP decreased southwards from about 0.2 $\mu\text{mol L}^{-1}$ to less than 0.1 $\mu\text{mol L}^{-1}$. The relative proportion of TDP as DOP also decreased along this transect from 60% to 30% of the TDP pool (Vidal et al., 1999). The increasing northward trend appears to

continue, as Cavender-Bares et al. (2001) reported that DOP comprised more than 90% of TDP in the North Atlantic between 26°N and 37°N. Given that ambient DOP concentrations are a result of the balance between production (or release through cell lyses) and degradation of DOP, ascertaining the underlying reasons for these contrasting spatial trends in the North Atlantic and North Pacific will require comparisons among N and C dynamics as well as perhaps plankton speciation in these regions.

Although dissolved organic C (DOC) and N (DON) concentrations were not measured in our samples, the increase in DOP concentrations from the subtropical frontal zone to the subarctic region (Fig. 2E) is opposite to the reported trend for DOC concentrations (Abell et al., 2000; Hansell, 2002). In contrast, the variation of TON (comparable to DON) concentration is similar to that of TOP (comparable to DOP) between the subarctic frontal zone and middle of the subtropical region; however the variations of TON and TOP were uncoupled between middle of the subtropical region and the equatorial transition zone in the North Pacific (Abell et al., 2000). This apparent uncoupling of DOC, DON and DOP distribution, if verified, could be a result of interactions with substrates and dissolved inorganic nutrients through bacterial and phytoplanktonic activity. Comprehensive studies including not only inorganic nutrients but also dissolved organic matter are necessary for understanding the biogeochemical cycle of C, N and P.

The results of this study reveal that both the size of the DOP pool and the proportion of TDP as DOP differed between the subtropical frontal zone through the subarctic region. Similarly, the quality of DOP also likely differs between low latitudinal regions having a high DOP demand and high latitudinal regions having a low DOP demand. Both the differences in bulk DOP concentrations and the differences in DOP production/decomposition processes in the subtropical region through the subarctic region should be addressed in future studies. Additionally, N_2 fixation is recognized as a key process in the tropical and the subtropical regions (Karl et al., 1997). Phosphorus availability (along with Fe) then will serve as a keystone variable in controlling nutrient cycling and C sequestration (Sañudo-Wilhelmy et al., 2001; Mills et al., 2004), leading to the need for a better understanding of DOP dynamics in seawater.

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