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Phosphate availability and the ultimate control of new nitrogen input by nitrogen fixation in the tropical Pacific Ocean

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Abstract

Due to the low atmospheric input of phosphate into the open ocean, it is one of the key nutrients that could ultimately control primary production and carbon export into the deep ocean. The observed trend over the last 20 years, has shown a decrease in the dissolved inorganic phosphate (DIP) pool in the North Pacific gyre, which has been correlated to the increase in di-nitrogen (N_2) fixation rates. Following a NW-SE transect, in the Southeast Pacific during the early austral summer (BIOSOPE cruise), we present data on DIP, dissolved organic phosphate (DOP), and particulate phosphate (PP) pools and DIP turnover times (T_{DIP}) along with N_2 fixation rates. We observed a decrease in DIP concentration from the edges to the centre of the gyre. Nevertheless the DIP concentrations remained above 100 nmol L^{-1} and T_{DIP} were more than a month in the centre of the gyre: DIP availability remained largely above the level required for phosphate limitation. This contrasts with recent observations in the western Pacific Ocean at the same latitude (DIAPALIS cruises) where lower DIP concentrations (<20 nmol L^{-1}) and T_{DIP}<50 h were measured during the summer season. During the BIOSOPE cruise, N_2 fixation rates were higher within the cold water upwelling near the Chilean coast. This observation contrasts with recently obtained model output for N_2 fixation distribution in the South Pacific area and emphasises the importance of studying the main factors controlling this process. The South Pacific gyre can be considered a High P Low Chlorophyll (HPLC) oligotrophic area, which could potentially support high N_2 fixation rates, and possibly carbon dioxide sequestration, if the primary ecophysiological controls, temperature and/or iron availability, were alleviated.

1 Introduction

New nitrogen (N) input by N_2 fixation has been recognized as a significant process influencing global oceanic productivity and the associated carbon fluxes (Karl et al., 1997; Falkowski, 1997). It is the primary process responsible for the input of N-containing

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compounds into the sea (Codispoti et al., 2001; Capone and Knapp, 2007) and can decouple N from other bioelement cycles which depend on ocean mixing; this decoupling has potentially important biogeochemical implications (Gruber, 2004; Karl, 2007). This input largely depends on the biomass of N_2 fixing organisms, which in turn depends on factors such as temperature (Capone et al., 1997; Staal et al., 2003; Breitbarth et al., 2007), iron (Falkowski, 1997; Kustka et al., 2002; Fu and Bell, 2003) and P availability (Karl et al., 1997; Sanudo-Wilhelmy et al., 2001; Moutin et al., 2005; Karl et al., 2007) and even on the carbon dioxide concentration in areas where light and nutrients, such as P or iron (Fe), are not limiting (Levitan et al., 2007). These factors are affected by human activity (increase in temperature, nutrient input by rivers and atmospheric Fe input), so the input of N, via N_2 fixation, may change over time. Indeed, Karl et al. (1997) have observed an increase in diazotrophic populations at the ALOHA station, in the Subtropical North Pacific gyre, along with a decrease in soluble reactive P (SRP which is equivalent to DIP in our study) and an apparent shift from N limitation to P limitation (Karl et al., 2001). A major result from the ALOHA station has been the discovery of a 17 year drawdown for DIP and particulate P (PP), which is consistent with enhanced new production by N_2 fixation (Karl, 2007).

P availability is a crucial factor in controlling the process of N_2 fixation. It has long been considered, by "geochemists", as the ultimate factor controlling primary production in the global ocean (Redfield et al., 1963; Tyrrell, 1999). Contrary to N, there is no atmospheric reservoir of P so there is no alternative source when P runs out. Furthermore, P availability in the open ocean is probably less affected by human activity. P coming into the sea is mainly of river origin (Broecker and Peng, 1982). Here levels of P are also increasing (Meybeck, 1993; Moutin et al., 1998), however, due to its rapid consumption by biological or chemical processes in estuaries (Lucotte and Danglejan, 1988; Golterman and de Oude, 1991), P input by rivers, may have little impact on a global scale, at least over a decadal time scale. Most P is trapped in the superficial sediment (Van Den Broeck and Moutin, 2002; Paytan and McLaughlin, 2007) and may only have local impact. Thus, it is necessary to determine the current P availability in

the open ocean to determine its role in the control of N_2 fixation, at the present time and in the near future.

We studied N_2 fixation, P pools and subsequent nutrient availability for planktonic species, following a NW-SE transect in the South Pacific Ocean during November–December 2004 (BIOSOPE cruise). N_2 fixation, DIP, DOP and PP pools were measured together with DIP turnover times in the upper water column. Data from this cruise, particularly from the central gyre, which is one of the least studied major oceanic entities of the worlds ocean, is compared with data obtained from the North Pacific gyre at the ALOHA station and a station in the South Western Pacific, where blooms of the N_2 fixing cyanobacterium *Trichodesmium*, are frequently observed (Dupouy et al., 2000). The recently described unicellular cyanobacteria (Zehr et al., 2001, 2007) further emphasises the importance of the N_2 fixation process in the budget of new N. Nevertheless, current estimates suggest that *Trichodesmium* may be two- to threefold more abundant than previously reported and may account for the missing sink of ~90 Tg N required to support the observed new production in the ocean (Davis and McGillicuddy, 2006; Levitan et al., 2007) and confirms the prevalent role of *Trichodesmium* previously reported "in the oligotrophic ocean" (Capone et al., 1997). We consider the current understanding of the factors controlling N_2 fixing organism biomass and the most probable temporal evolution of these factors, and then discuss the predictable changes that may occur in N_2fixation and DIP availability in the South equatorial Pacific.

2 Methods

2.1 Station locations, cruises, chronology and sample collection

The BIOSOPE cruise was carried out during November–December 2004 from the Marquesas Islands to the Chilean coast (Fig. 1). We sampled water along a 6000 km transect and the clearest ocean waters, near Easter Island (Morel et al., 2007) inside the South East Pacific gyre suggested to be the most oligotrophic and stable water body

on the basis of remotely sensed ocean color (Claustre and Maritorena, 2003). All samples were collected from a CTD rosette fitted with 20, 12-L Niskin bottles equipped with silicone rubber closures and tubing that had been carefully cleaned to avoid introducing toxic metals during sampling. Following water collection, samples were processed within 1 h.

Data from the central station, inside the South Pacific gyre (S-gyre station), are compared with data obtained from the DIAPALIS cruises, at the chenal des Loyauté station (SW station) in 2002–2003, and data from the ALOHA station (N-gyre station) in the North Pacific in 2000–2001 (Table 1 and Fig. 1).

2.2 Analytical methods

2.2.1 N_2 fixation

One mL of $^{15}N_2$ gas (99% $15N_2$ EURISOTOP) was introduced to each 0.6 L polycarbonate bottle through a Teflon-lined butyl rubber septum using a gas-tight syringe, following the protocol of Montoya et al. (1996). Following 24 h incubations, the samples were filtered under low vacuum (100 mm Hg) through precombusted (24 h at 450°C) 25-mm GF/F filters and dried at 60°C. Filters were stored in a desiccator until processed. Determination of ^{15}N enrichments were performed using an Integra-CN PDZ EUROPA mass spectrometer. We have considered a background natural abundance, determined on 8 unlabelled samples, of 0.367±0.007%. Only excess enrichments higher than two times the standard deviation (0.014% for N) were considered significant. As we worked with low levels of particulate N (PN), we have calibrated the spectrometer using the same conditions as for PN and the quality of the analysis was tested with standard molecules (glycine). Based on the lowest N level determined by our mass spectrometer (0.2 μmol), the detection limit for N_2 fixation was 0.12 nmol L^{-1} d^{-1}. N_2 fixation rates (nmol L^{-1} d^{-1}) were computed from an equation based on final PN (Dugdale and Wilkerson, 1986).

2.2.2 P pools

Total P (TP) in seawater samples may be separated in three pools: the Dissolved Inorganic P (DIP) pool, the Dissolved Organic P (DOP) pool and the Particulate P (PP) pool.

The DIP pool was estimated on board using the molybdenum blue reaction (Strickland and Parsons, 1972), on 50 mL samples, using a 10 cm length-cuvette in a spectrophotometer (Cecil CE 1011), at 880 nm, following 30 min reaction time. Concentrations were expressed in nmol L^{-1}. The lower limit of detection for DIP by this method was 20 nmol L^{-1}. The new MAGIC 25 procedure (Rimmelin and Moutin, 2005) was also conducted on triplicate samples at the S-gyre station to determine DIP concentration (detection limit = 0.8±0.5 nmol L^{-1}) and the arsenate concentration. The arsenate concentration was 10.8 nmol L^{-1} (sd=8.6, n=21). Because it is lower than the detection limit of the Strickland and Parsons (1972) procedure to measure DIP and not constant (relatively high standard deviation), no arsenate correction was taken into account for this measurement.

The PP pool was determined by the filtration of 1-L samples through polycarbonate filters (0.2 μm; 47 mm). PP was measured by standard DIP analysis, at 880 nm, following high temperature persulfate wet-oxidation at 120°C and 1 bar (Pujopay and Raimbault, 1994) which converts all inorganic and organic non-reactive P compounds to DIP.

Total P (TP) was estimated on 40 mL duplicate samples of seawater, using the same high-temperature persulfate wet-oxidation pre-treatment as for PP. DIP was then analysed as previously described. The measurement of DOP in seawater requires simultaneous measurements of DIP and TP. DOP was assumed to be equal to ([TP]–[DIP+PP]). The precision and accuracy of the DOP estimates decreased with increasing depth, as DIP concentrations became the dominant component in the total dissolved nutrient pools.

2.2.3 Turnover times of DIP

The DIP turnover time (T_{DIP}) corresponds to the ratio of DIP concentration to DIP uptake. Thingstad et al. (1993) derived the following relationship for T_{DIP}: $r(t)=1-e^{-t/T}$, where r is the fraction of added radioactivity absorbed, t the incubation time and T the turnover time. This equation has been rearranged in order to give a direct calculation for turnover time: $T=-t/\ln(1-R(t))$ where $R(t)=(R_f-R_b)/R_t$, R_f, the radioactivity on the filter, R_b, the radioactivity of the blank, and R_t, total tracer added. T_{DIP} was determined using ^{33}P tracer (H_3PO_4 in dilute hydrochloric acid; Amersham BF 1003; specific activity >3000 Ci mmol^{-1}). The working solution of ^{33}P-DIP was prepared by diluting the tracer in Milli-Q water filtered on pre-washed 0.2 μm filters, immediately before use. 300 mL of seawater was dispensed into acid-washed, Milli-Q and sample rinsed polycarbonate bottles, and incubated with 25 μCi carrier-free $^{33}PO_4$ of working solution to give a total activity of 0.08 μCi mL^{-1}. Less than 0.03 nmol L^{-1} of P was added to each sample. The bottles were then placed in an on-deck incubator and maintained at constant temperature using a continuous circulation of surface seawater, at 50, 25, 15, 7, 3 and 1% incident light. The same protocol was used for duplicate 300 mL samples where 300 μL $HgCl_2$ (20 g L^{-1}) had been added as a control for non-biological uptake. Incubations were stopped by the addition of 600 μL of non-radioactive KH_2PO_4 (10 mmol L^{-1}). The optimal incubation time (4 to 5 h) was determined from a prior time-series experiment. Ideally, sample counts should be at least 10 times greater than the blanks, less than 10% of the radioactivity in the samples should be consumed, and incubations should not exceed several hours in order to minimize the increase in bacterial production caused by confinement (Van Wambeke et al., 2007[1]). DIP turnover time was measured in 50 mL duplicate sub-samples from each bottle. Filtrations were carried out on 25 mm polycarbonate filters (0.2 μm), placed on

[1]Van Wambeke, F., Obernosterer, I., Moutin, T., Duhamel, S., Ulloa, O., and Claustre, H.: Heterotrophic bacterial production in the South East Pacific, Biogeosciences Discuss., submitted, 2007.

DIP-saturated support GF/F filters, using a low-vacuum pressure <0.2 bars. Filters were not washed with filtered seawater at the end of the filtration, but pressure was briefly increased to 0.6 bars, to remove non cellular radioactivity from the filter. Filters were then placed in low-potassium 6 mL glass scintillation vials (Wheaton) with 6 mL of scintillation liquid (Ultima gold MV, Packard) and the radioactivity of the filters measured using a scintillation counter Packard Tri-Carb® 2100TR. Initial radioactivity was measured on 5 replicates of 5 μL of working solution in parallel of each experiment to verify the amount of ^{33}P added to each sample.

2.2.4 Labile DOP

We used the Strickland and Parsons (1972) procedure to measure the labile DOP within the gyre. This pool was assumed to be mainly composed by P monoesters and thus, to be easily hydrolysed by alkaline phosphatase. At each station from the NW edge to the centre of the gyre, a 50 mL triplicate surface (50% of incident light depth) sample was incubated with 1 mL of a fresh and pure solution of *Escherichia coli* alkaline phosphatase (Sigma P-4252, 0.2 U mL^{-1}) and 1 mL of Tris buffer solution 0.5 M (pH=8). After 2 h of incubation at 30°C, the DIP concentration was measured. Another triplicate of surface sample was processed in parallel in order to determine the initial DIP concentration. The labile DOP concentration is the difference between these two measurements. For each series of measurements, a blank sample was processed as well as a control with 1 μmol L^{-1} of a glucose-6-phosphate solution in order to confirm enzymatic efficiency.

2.2.5 Excess DIP relative to nitrate concentration

Ambient nitrate + nitrite and nitrite were immediately measured after collection by directly pumping with the Technicon AutoAnalyzer in the sampling polyethylene bottle. Nitrate and nitrite concentrations in the nanomolar range (lower detection, 3 nmol L^{-1}) were obtained from a sensitive method according to Raimbault et al. (1990). For sub-

micromolar concentrations, the classical Technicon AutoAnalyser method was used (Tréguer and LeCorre, 1975). The recently defined variable P* (Deutsch et al., 2007) was calculated: P*=[PO_4]–[NO_3]/rr (rr = Redfield ratio = 16), [PO_4]=DIP in this study.

3 Results

3.1 P pools and DIP turnover times in the South Pacific gyre

3.1.1 Spatial distribution

DIP, DOP and PP concentrations in surface waters were highest near the Marquesas Islands and near the Chilean coast (Figs. 2a, b, c). For the 3 distinct pools, there is a clear decrease in concentration from the edge to the centre of the gyre, reaching minimum values of 120 and 150 nmol L^{-1} for the DIP and DOP pools respectively, and less than 10 nmol L^{-1} for PP. Duhamel et al. (2007) have argued that the PP pool is mainly associated with living biomass in the centre of the gyre. Values of PP less than 10 nmol L^{-1} were measured, which suggests extremely low biomass (Duhamel et al., 2007). In the upper layer from the edge to the centre of the gyre, the decreases in concentrations of DIP and PP are approximately an order of magnitude compared to a factor of 2.5 for the DOP pools. The DIP/DOP concentration ratio is close to one in the centre of the gyre. The labile DOP concentrations (P monoesters) inside the gyre at 5 meter depth were 4.7 nmol L^{-1} (sd=15.0, n=8), i.e. close or below the detection limit of 20 nmol L^{-1}. DIP turnover times varied from several days on the edge, to around 200 days in the gyre (Fig. 2e). Higher P* values were observed near the Chilean coast under a 100 m depth (~1000 nmol L^{-1}) and close to the Marquesas Islands (~500 nmol L^{-1}). Values of less than 200 nmol L^{-1} were observed in the centre of the South Pacific gyre (Fig. 2f) where the nitrate concentrations became <3 nmol l^{-1} (Fig. 2d).

3.1.2 Vertical depth profile inside the gyre (S-gyre station)

DIP concentrations are homogeneous having a mean value of 127.0 nmol L^{-1} (sd=7.1, n=42) in the surface waters (0–150 m) and increasing with depth below 150 m (Fig. 3b) at the S-gyre station. The DIP concentration versus depth gradient between 150 and 250 m is 3.5 μmol m^{-4}. DIP concentrations in surface waters are above the detection limits of the standard method (Strickland and Parsons, 1972). No significant difference was observed with the high sensitivity MAGIC 25 method (Rimmelin and Moutin, 2005) thus enabling us to validate our detailed protocol for a 25 times MAGIC preconcentration procedure. DIP turnover times are homogeneous with a mean value of 273 days (sd=29, n=21) in surface waters (Fig. 3h).

DOP concentrations are highest in near surface waters with a mean value of 175.5 nmol L^{-1} (sd=9.2, n=21) and decrease with increasing water depth (Fig. 3f). DOP dominates in the surface water, accounting for 58% of the total dissolved P pool. DIP becomes the dominant component of the total dissolved pool below 150 m. The mean DOP concentration from duplicate deep water samples (600–2000 m) is 61.0 nmol L^{-1} (sd=16.5, n=8). PP concentrations follow the same pattern as DOP concentrations with a mean value of 9.3 nmol L^{-1} (sd=1.5, n=6) in surface waters decreasing as water depth increased (Fig. 3g). Values below 200 m were similar to the mean concentration from duplicate deep water samples (600–2000 m) of 1.0 nmol L^{-1} (sd=0.3, n=8).

3.1.3 Comparison with depth profiles from the SW and N-gyre Pacific stations

Trends with depth similar to those at the S-gyre station are observed for DIP, DOP and PP at the SW (Figs. 3a, b, c) and N-gyre (Figs. 3i, j, k) stations; the only exception is the sharp decrease in DIP concentration, observed in the SW station (Fig. 3a), during the summer period. The average decrease in DIP concentration between austral winter and austral summer in the upper 40 m of the water column was 35 nmol L^{-1} at the SW station. This difference corresponds to a minimum value as DIP concentration was

generally below the 20 nmol L^{-1} detection limit of the classical Strickland and Parsons (1972) method. No MAGIC measurements are available but indirect estimations of the DIP concentrations from T_{DIP} measurements (Van Den Broeck et al., 2004) indicated sub-nanomolar concentrations during the summer period. There was no corresponding increase in either the PP pool or the DOP pool, although large differences in the concentration of the DOP pool were observed during both the winter and summer periods. DIP turnover times (Fig. 3d) vary from approximately 10 days in winter to a few hours in summer in near surface waters.

No clear seasonal variations were observed in the DIP pool at the N-gyre station (ALOHA, Fig. 3i). DIP concentrations were lower (by a factor of 2–2.5) than concentrations measured in the mixed layer of the S-gyre station. DOP concentrations were slightly above the DOP concentrations measured in the S-gyre station and very close to those measured at the SW station. The PP concentrations at the N-gyre station were higher (by a factor of 1.5) than those in the more oligotrophic S-gyre station. DIP turnover times were around 10 days near the sea surface, close to those observed during the winter season at the SW station and no marked variations between the summer and winter seasons are observed.

3.2 Current distribution of N_2 fixation

The N_2 fixation gave maximum values, around 4 nmol L^{-1} d^{-1}, near the Chilean coast, intermediate values near the Marquesas Islands and low values, just above the detection limit of the method employed (0.12 nmol L^{-1} d^{-1}), inside the gyre (Fig. 2g). Integrated depth profiles gave a value of ~142 μmol N m^{-2} d^{-1} near the Chilean coast (1 in situ depth profile between 0 and 40 m) and 48 and 135 μmol N m^{-2} d^{-1} at the S-gyre station (2 in situ depth profiles between 0 and 200 m). Maximum N_2 fixation rates were found in the upwelling area where low N:P ratio waters (Fig. 2h) and ample Fe concentrations are found, and temperatures did not exceed 16°C. The N_2 fixation rates are maximum near the surface within the gyre and decrease with depth mean-

ing that light might play a role in the control of this flux. At present we do not know the species responsible for these fluxes. *Trichodesmium*, a large filamentous N_2 fixing microorganism that often forms large easily identified colonies, was not observed.

The N_2 fixation rate at the SW station was highly variable within seasons and ranged between 151–703 μmol N m^{-2} d^{-1} (Garcia et al., 2007). The maximum value corresponds to a *Trichodesmium* specific bloom that occurred during the summer period when temperatures were above 26°C. At the N-gyre station ALOHA, higher N_2fixation rates than those measured in the South Pacific gyre have already been reported and these appear to be associated with *Trichodesmium* blooms (Karl et al., 1992; Dore et al., 2002). At least two independent microbial assemblages and ecosystem processes contribute to N_2 fixation in the NP gyre, namely the "background state" wherein a relatively low but relatively constant rate supported by pico and nano-diazotrophs, and the aperiodic "bloom state" wherein large filamentous, colonial and aggregate forming diazotrophs (*Trichodesmium* and/or endosymbiont-containing diatoms) dominate the new N cycle (Karl et al., 2007). Dore et al. (2007)[2] estimated that the summer bloom is responsible for up to 38% of the annual N_2 fixation at ALOHA station. Based on a variety of independent estimates including nitrogenase activity by acetylene reduction method, *Trichodesmium* abundance, N:P mass balance, and ^{15}N isotope balance, an annual N_2 fixation rate of 31–51 mmol N m^{-2} $year^{-1}$ was estimated for the Pacific Ocean near Hawaii (Karl et al., 1997). N_2 fixation at Station ALOHA would equate to 3–4% of the total N demand for the microorganisms that inhabit that ecosystem however, when compared to estimates of new production or to N exports by sinking particles and migrant zooplankton, N_2 fixation appears to be a significant (40–60%) source of new N (Karl et al., 2007) since export from oligotrophic ecosystems is low. When compared to estimates of new production with ^{15}N, N_2 fixation accounted for up to 50% in the South

[2]Dore, J. E., Letelier, R. M., Matthew, J., Churcha, M. J., Lukasa, R., and Karl, D. M.: Summer phytoplankton blooms in the oligotrophic North Pacific Subtropical Gyre: Historical perspective and recent observations, in preparation, 2007.

Pacific gyre (Raimbault and Garcia, 2007[3]).

4 Discussion

4.1 P availability in the contemporary ocean, regional habitat comparisons

4.1.1 Availability of DIP

DIP is directly available for all microbes and can be considered as the first criteria to evaluate P availability. DIP is not completely exhausted from the upper water at the N-gyre station (ALOHA) or in the South Pacific gyre, but DIP concentrations reach <20 nM concentration during the summer season at the SW station. As these DIP concentrations at the SW station are close to or even below chemical detection limits of classical chemical analyses (20 nM), the study of DIP turnover times can provide additional information on nutrient availability: DIP turnover time is the most broadly-applicable measurement of DIP availability because it has the potential to identify variation in P availability even when DIP concentrations become chemically undetectable (Moutin et al., 2002, 2005). DIP turnover times represent the ratio between DIP concentration and DIP uptake by the microbial assemblage. Despite the DIP concentrations being much lower in the centre of the South gyre than those found near the Marquesas Islands and Chilean coast, the larger T_{DIP} indicates that DIP availability, compared to the planktonic species requirement within the gyre, is greater than in the upwelling region. The turnover time is also the time it would take for all the ambient DIP to be taken up assuming no additional input (Ammerman et al., 2003). Without any additional external sources and input by regeneration, it would take 200 days to exhaust all available DIP in the gyre, while it may only take 10 days in the Chilean upwelling and at the N-gyre station (ALOHA). Nonetheless, T_{DIP} in the Southern and Northern

[3]Raimbault, P. and Garcia, N.: Carbon and nitrogen uptake in the South Pacific Ocean, Biogeosciences Discuss., submitted, 2007.

gyres suggest a P sufficiency that is contrary to what has been observed in the very P-depleted Mediterranean Sea, Sargasso Sea and South Western Pacific during the summer season (Table 2) where T_{DIP} below 10 h were observed (Table 2).

4.1.2 Availability of DIP and *Trichodesmium* growth

A critical DIP turnover time of 50 h, giving favourable and unfavourable growth conditions for *Trichodesmium*, was determined during the DIAPALIS survey in the SW Pacific ocean (Moutin et al., 2005). It was demonstrated that the sharp decrease in DIP availability in the early summer season could explain most of the numerous and periodic sea surface accumulations of *Trichodesmium* observed, and more importantly, the prevalent role of DIP availability in the control of N input by N_2 fixation in this area (Moutin et al., 2005). The DIP turnover times of around 10 days measured at the N-gyre station (ALOHA, Fig. 3l) suggests a higher P deficiency than in the South Pacific gyre (T_{DIP} around 200 days and DIP concentrations >100 nmol l^{-1}), but this is not strong enough to provoke *Trichodesmium* decay (obtained for T_{DIP}<50 h equivalent to DIP concentration <10 nmol l^{-1} at the SW station). Thus, another factor must prevent the complete exhaustion of DIP and may currently control N_2 fixation by *Trichodesmium* at the N-gyre station (ALOHA). Nevertheless, episodic *Trichodesmium* blooms followed by severe DIP depletion have already been observed at the N-gyre station (Letelier, ASLO meeting 2006). Short DIP turnover times of around 2 days have also been reported (Bjorkman et al., 2000, Table 2) and a long term decrease in DIP availability (Karl et al., 1997, 2001). The comparison between DIP turnover times obtained by Perry and Eppley (1981) in the central Pacific gyre in the 70's, and other current estimations (Table 2) confirmed the decrease in DIP availability, particularly during the summer season.

4.1.3 Availability of DOP

For the most part DOP is not directly available to living organisms as it cannot be taken into the cell in this form (Cembella et al., 1984; Bjorkman and Karl, 2003; Paytan and McLaughlin, 2007). Organic P must first be converted to DIP. The labile fraction of the DOP pool inside the South gyre was $<20\,\mathrm{nmol\,L^{-1}}$ suggesting that only a small fraction of the DOP pool was available (through alkaline phosphatase activity). At the SW station during the summer period, DIP concentrations reached $<20\,\mathrm{nmol\,L^{-1}}$ concentrations. However, no significant change was observed in the DOP concentrations (Fig. 3b), which suggests that most of the DOP pool in the upper surface is not readily available, even after several months of severe DIP depletion. Moreover, despite the variations in DIP concentrations and turnover times at all three stations, the DOP concentration was around $200\,\mathrm{nmol\,L^{-1}}$ at all of them suggesting that the DOP reservoir is not a particularly dynamic reservoir of P in upper ocean waters. The South Pacific gyre appears to be an ocean essentially at rest, or at least as close as can be expected (M. Lewis, personal communication). Thus, the DOP pool in the S-gyre station may mainly be an accumulation of older organic molecules with low bioavailability.

Even though most of the DOP pool is not readily available, it may play a determinant role in phytoplankton growth. It is probable that the turnover of the available DOP pool, even small, is rapid. It has been estimated that DOP utilization can be of the same order of magnitude as DIP utilization in the upper water column at ALOHA (Bjorkman and Karl, 2003). Recent evidence also indicates that certain compounds in the DOP pool, particularly the phosphonates, which may account for 25% of the high molecular weight DOP pool (Clark et al., 1998; Kolowith et al., 2001), may be used (Dyhrman et al., 2006), but we know little about its global significance and this is a major scope for future research in the field of P availability.

4.1.4 Availability of DIP pool vs. availability of DIN pool

P* is a convenient estimate of the excess in DIP relative to DIN, when these nutrients are assumed to be utilised following the Redfield proportions (N:P=16). P* variations in the South Pacific are close to those expected by Deutsch et al. (2007). They argue that denitrification in the oxygen minimum zones (OMZs) generate DIP-enriched and DIN- deficient waters that subsequently undergo a disproportionate loss of DIP as they are upwelled and transported into the adjacent gyres. The eastern Pacific Ocean near the Chilean coast is one of the three major areas of denitrification in the world oceans (Codispoti and Richards, 1976). Thus, it may explain the high P* observed (right part of Fig. 2f). North of 14° S, the waters are under the influence of the equatorial regime (Claustre et al., 2007[4]). Following general circulation models, water near the Marquesas Islands (left part of Fig. 2f) are influenced by waters upwelled near the equator. This may also explain the high P* value observed in this area. The decrease in P* toward the centre of the gyre corresponds to the already observed trend by Deutsch et al. (2007): downstream of OMZs, surface waters that initially carry a surplus of phosphorus (because of subsurface denitrification) loose this excess gradually through N_2fixation. They attribute this effect to N_2 fixation restoring the system to a "Redfieldian" balance (Redfield, 1934; Capone and Knapp, 2007).

4.2 N_2 fixation distribution and controls other than P availability

The model by Deutsch et al. (2007) for N_2 fixation rates along the studied transect, with minimum values found on the edge and maximum values in the centre of the gyre, is contrary to our observations. They calculated a basin-wide N_2 fixation rate for the Pacific of 48 mmol N m^{-2} yr^{-1} (similar to previous estimates ~50 mmol N m^{-2} yr^{-1},

[4]Claustre H., Sciandra, A., Vaulot, D., and Raimbault, P.: Introduction to the special section: bio-optical and biogeochemical conditions in the South East Pacific in late 2004 – the BIOSOPE program, Biogeosciences Discuss., in preparation, 2007.

Redfield et al., 1963), with maximum values, up to 120 mmol N m^{-2} yr^{-1} inside the South Pacific gyre. Assuming no seasonal variations (i.e. 120 000/365~330 μmol N m^{-2} d^{-1}) and a maximum depth of 200 m available for N_2 fixation inside the gyre, this rate is equivalent to 1.7 nmol N L^{-1} d^{-1}, a value at least 2.5 times greater than the mean rate that we measured (0.24 and 0.67 nmol N L^{-1} d^{-1}). The annual rate calculated near the Chilean coast by Deutsch et al. (2007) is under 20 mmol N m^{-2} yr^{-1}. Assuming no seasonal variations (i.e. 20 000/365~55 μmol N m^{-2} d^{-1}) and a maximum depth of ~40 m available for N_2 fixation in the upwelling, this rate is equivalent to ~1 nmol N L^{-1} d^{-1}, a value around 4 times below the measured value. Thus, even if the P* distributions calculated (Deutsch et al., 2007) and observed (Fig. 2f) are very similar, the distributions of N_2 fixation in the South Pacific gyre are not consistent with predicted rates. Some of this discrepancy is certainly due to uncertainties in ocean circulation. It is more likely to be related to the controlling factors of N_2 fixation i.e. temperature, Fe availability and N:P ratios. Indeed, N_2 fixing biomass-P and biomass-Fe requirements must be provided by the upper photic water column, and the temperature must be adequate to enable growth or N_2 fixation.

4.2.1 Temperature

Temperature per se does not restrict diazotroph growth; N_2 fixers can be encountered at temperatures close to freezing (Zielke et al., 2002; Pandey et al., 2004). However, there are numerous studies showing a correlation between *Trichodesmium* abundance and temperature (Capone et al., 1997; Lugomela et al., 2002; Chen et al., 2003; Moutin et al., 2005). The relationship between *Trichodesmium* distribution and sea surface temperature (SST) is so "commonly accepted" that the observed temperature distribution range (20–30°C) is used to constrain N_2 fixation in oceanic biogeochemical circulation models (OCBM) (Fennel et al., 2002; Hood et al., 2004). Temperatures above 26°C are necessary for *Trichodesmium* bloom development (Carpenter et al., 2004). The correlation between water temperature and *Trichodesmium* abundance is

generally attributed to oceanographic features associated with warm waters, such as a shallow mixed layer, high light regimes and oligotrophic nutrient conditions, rather than to a direct physiological response to the temperature itself (Hood et al., 2004). Nevertheless, it was recently demonstrated that the *Trichodesmium* strain IMS-101 are adapted to optimum growth temperatures of between 24 and 30°C tolerating temperatures from 20 to 34°C (Breitbarth et al., 2007). Thus, as suggested by Capone et al. (1997), seawater temperature sets a physiological constraint on the geographical distribution of *Trichodesmium* (Breitbarth et al., 2007).

Staal et al. (2003) showed that differences in the temperature dependence of O_2 fluxes explained how *Trichodesmium* performs better than heterocystous species at higher temperatures. They provide an explanation for the exclusion of free-living heterocystous cyanobacteria in the N-depleted euphotic zone of the pelagic tropical ocean, although this explanation needs to be reconsidered against recent N_2 fixing organism abundance measurements (Zehr et al., 2007).

Most of the numerous sea surface accumulations of *Trichodesmium* observed in the South western Pacific Ocean near New Caledonia occurred during the spring and early summer periods when temperatures were above 25°C. It is related to the end of the bloom and is caused by P deficiency (Moutin et al., 2005). Monthly, mean SST's reached a maximum of 25.1°C during summer at the S-gyre station reaching 27.3 and 26.4 C at the SW and N-gyre Pacific stations, respectively. SST's were less than 20°C over a large part of the South Pacific gyre during the BIOSOPE cruise (Claustre et al., 2007) and may explain the absence of *Trichodesmium*.

4.2.2 Fe availability

Numerous experimental studies attribute a dominant role of Fe availability in the control of diazotrophs growth (Paerl, 1994; Falkowski, 1997; Kustka et al., 2002; Mills et al., 2004). A high Fe requirement of the enzyme nitrogenase is believed to prevent N_2 fixing organisms from alleviating widespread N limitation (Falkowski, 1997). Atmospheric input of dust, which is highly concentrated in Fe relative to other nutrients,

plays a significant role in the distribution of *Trichodesmium* (Orcutt et al., 2001) and on the uncoupling between N-P-Fe-Si biogeochemical cycles in the ocean (Karl, 2002). High rates of N_2 fixation in the North Atlantic were considered to be the result of the unusually high growth rates of N_2 fixers, stimulated by the high Fe availability (Wu et al., 2000; Deutsch et al., 2007). Contrary to the oceanic gyres situated in the Northern Hemisphere, Fe-rich dust deposition is extremely low in the South Pacific gyre (Wagener et al., 2007[5]) and dissolved Fe concentrations of $0.13 \pm 0.03\,\mathrm{nmol\,l^{-1}}$ inside the upper water (0–80 m) of the gyre (Blain et al., 2007) may prevent the development of *Trichodesmium*. Nevertheless, enrichment experiments showed that primary production was N-limited at the S-gyre station and no nitrogen fixation was measured after dust, Fe and/or P additions (Bonnet at al., 2007).

4.2.3 N:P ratios

Deutsch et al. (2007) provide evidence that biological N_2 fixation is intimately associated, both geographically and temporally, with marine N removal (Capone and Knapp, 2007). Furthermore, their work implies that the ratio of N to P in seawater may be the central factor regulating N_2 fixation and that Fe rich dust may not exert as much influence on marine N_2 fixation (Capone and Knapp, 2007) as is currently assumed (Berman-Frank et al., 2001). The strong relationship between P* and N_2 fixation rates observed (Figs. 2f and g) may further strengthen the idea that biological N_2 fixation and marine N removal are tightly coupled (Deutsch et al., 2007): N_2 fixation begins, and is highest, when upwelled waters reach the surface near the Chilean coast. The waters don't need to be transported to the warmer adjacent gyre to loose most of their excess P. N_2 fixation in the surface waters results in the net biological uptake of DIP that occurs in the absence of a stoichiometric uptake of nitrate (~DIN), which increases the deficit in DIP relative to DIN (decrease of P*). However, N_2 fixation is not the only

[5]Wagener, T., Guieu, C., Losno, R., Bonnet, S., and Mahowald, N.: Revisiting Atmospheric dust export to the South Hemisphere Ocean, Global Biogoechem. Cycles, in review, 2007.

process driving the decrease in P* in the water. The export of material with a N:P ratio lower than the Redfield ratio will give the same pattern. It is not known whether the greater depth of the new production synthesis outside the upwelling produces exported material with a higher P content. The close link between denitrification and N_2 fixation is convincing but another simple explanation for the higher N_2 fixation rates near the Chilean coast could be that there is less competition for nutrients so enabling N_2 fixing organisms to thrive, independently from the DIN:DIP ratio.

4.3 P availability and the ultimate control of N_2 fixation in the tropical Pacific ocean

Following the most probable temporal changes (few decades) of the factors controlling N_2 fixation, several scenarios have been considered for N input via N_2 fixation and the ultimate P availability for the South Pacific Ocean:

4.3.1 Increase in temperature

The expected increase in temperature will increase stratification but probably not modify the upwelling intensity near the Chilean coast and thus, changes in N_2 fixation will likely occur elsewhere. If the presence of Trichodemium spp. is controlled by seawater temperature, any increase in temperature will increase its distribution. Breitbarth et al. (2007) predicted an 11% areal increase of *Trichodesmium*'s potential geographic distribution following a modelled SST increase of up to 3°C by 2090, but a simultaneous decrease in the area characterized by optimum growth. High SSTs are predicted for the western Pacific which is a characteristic province for present-day *Trichodesmium* abundance (LaRoche and Breitbarth, 2005). In this area where *Trichodesmium* biomass is already controlled by P availability, no change in N_2 fixation with increasing temperature is expected. Nevertheless, the increasing widespread high sea surface temperature is expected to increase the distribution area of *Trichodesmium* driving the system towards the ultimate P control over a larger area. An increasing trend in N_2 fixation associated with a decreasing trend in P availability may therefore be expected in the South tropical

Pacific ocean.

4.3.2 Increase in Fe dust deposition

The dominant external input of Fe to the surface of the open ocean is the transport of aeolian dust, from the great deserts of the world (Jickells et al., 2005) and this appears to be very sensitive to climate changes (Mahowald et al., 2006). The effect of dust/Fe in subtropical gyres is a reduction in Fe limitation on N_2 fixation so increasing primary production (Falkowski et al., 1998). A higher Fe supply to the sea surface has been hypothesized to favour N_2 fixation in the continentally influenced Atlantic Ocean (Wu et al., 2000) as well as in the South Western Pacific Ocean (Van Den Broeck et al., 2004) and probably the Mediterranean Sea. The increasing atmospheric input of Fe in the Northern Hemisphere has been assumed to explain the decreasing trend of P availability at the N-gyre station ALOHA (Karl et al., 2001). A similar trend may be expected for the South Pacific.

4.3.3 An extension of the geographical area of denitrification

Deutsch et al. (2007) suggest that N_2 fixation is closely coupled to the generation of N-deficient waters in areas of denitrification (timescale of year to decades) and are mainly dependent on the N:P ratios of the water upwelled near the coast. As denitrification occurs mainly in suboxic zones with $[O_2]<5\,\mu\text{mol}\,L^{-1}$ (Codispoti et al., 2001), any change in the spread of these areas will have significant impact on the N_2 fixation rate inside the gyres. The most probable future change is an extension of the geographical areas of denitrification. Thus, it will generate a higher volume of DIN deficient waters and consequently, according to Deutsch et al. (2007) a higher N_2 fixation rate in the South Pacific and a strengthening control of the carbon cycle by P availability.

5 Conclusion

We found that P availability was largely above the level required for P limitation on N_2 fixation in the South Pacific gyre. This is in contrast to recent observations in the SW Pacific Ocean over the same latitude. We suggest a geographical trend for limitation on N_2 fixation, from P limitation in the West to temperature and/or Fe limitation in the central and South East Pacific Ocean. The South Pacific gyre can be considered a High P Low Chlorophyll (HPLC) oligotrophic area, which could potentially support high N_2 fixation rates if the primary control temperature and/or Fe availability were alleviated. A decrease in P availability due to an increasing input of N by N_2 fixation is the most probable decadal trend to occur following climate change.

As already mentioned by Deutsch et al. (2007), environmental controls on N_2 fixation and thus its probable response to past and future climate change would be much clearer if we knew the geographic distribution of this process in the ocean. The poor correlation between their model output and our observations for N_2 fixation in the South Pacific area emphasise the importance of studying the geographical distribution of N_2 fixation as well as the main factors controlling this process. Increased understanding of the factors controlling the growth and biomass of N_2 fixing organisms is needed in the field in order to constrain the models.

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Table 1. SST range (°C, monthly long-term mean data), and integrated (0–100 m) P pools (mmol m^{-2}) at the three studied stations. *NOAA_OI_SST_V2 data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.cdc.noaa.gov/.

		SW station 21°30 S; 167° E	N-gyre station (ALOHA) 22°45 N; 158° W	S-gyre station 26°05 S; 114° W
SST (°C) range*	Min-Max	23.1-27.3	23.4-26.4	20.7-25.1
I DIP (0-100 m)	Winter-Summer	9.65-5.40	5.07-5.06	12.45
I DOP (0-100 m)	Winter-Summer	26.45-21.35	21.66-23.69	16.28
I PP (0-100 m)	Winter-Summer	1.97-1.52	1.44-1.33	0.54

Table 2. DIP turnover time (mean and standard deviation in hours) in upper ocean surface waters (0–20 m or at the depth of 50% of incident light*), D5S1N5 is for 5 depths (D5), 1 station sampled (S1), 5 samples (N5), as an example. ** = median value. See also Tanaka et al. (2006) for others T_{DIP} measurements in the Mediterranean Sea.

Winter	Spring	Summer	Fall	Area	Year of sampling	References
				Mediterranean Sea		
396 (370) D1S9N9	3,9 (2,4) D1S17N17	1,6 (0,9) D1S20N20		Lion gulf	1997-1998	Moutin et al (2000)
			10,5 & 7,6 D1S2N2	Alboran	1999	Moutin et al (2002)
			1,7 (1,5) D1S5N5	Western basin	1999	Moutin et al (2002)
			1,2 (0,5) D1S4N4	Eastern basin (Ionian)	1999	Moutin et al (2002)
2,9 & 6,7 D1S2N2				Eastern basin (Ionian)	1996	Zohary and Robarts (1998)
4,1 (1,6) D1S5N5				Eastern basin (Levantin)	1996	Zohary and Robarts (1998)
				Atlantic Ocean		
11 D1S1N1		5 D1S1N1		Sargasso Sea (BATS)	1992-1993	Cotner et al (1997)
230 (38) D1S3N3	1,3 (0,4) D1S4N4		217 D1S1N1	Gascogne gulf		Labry et al (2002)
			82 (25) D3S1N3	Marocco upwelling	1999	Moutin, unpublished
1182 (382) D2S3N6	152 (55) D2S4N8		168 (110) D2S4N8	North Eastern (between Azore islands and Spain)	2000-2001	Moutin, unpublished
				Pacific Ocean		
504 (175) D5S1N5	107 (37) D5S1N5	10,8 (2,4) D3S2N6	4,0 (0,3) & 68 (2) D5S1N5	South Western	2002-2003	Van den Broeck et al (2004)
672** S5	456** S6	744** S4		Northern central (within a degree of 30°N, 155° W)	1973-1974	Perry and Eppley (1981)
	504 (399) D1S1N3	144 D1S1N1	72 D1S1N1	Northern central gyre (ALOHA)	1996-1997	Björkman et al (2000)
	216 & 48 D1S2N2			Northern central gyre (Climax)	1996-1997	Björkman et al (2000)
514 & 500 D2S1N2	291 (36) D2S3N6	93 (35) D2S2N4	405 (31) D2S2N4	Northern central gyre (ALOHA)	2000-2001	Björkman et al (2003)
149 D1S1	120 D1S2	221 D1S1		Northern central gyre (ALOHA)	2002-2004	Van Mooy, unpublished
	936 (451) D1S3N6			South equatorial (Marqueous Island)	2004	This study*
	2086 (1202) D1S5N10			Western transition area	2004	This study*
	5589 (1472) D1S8N16			Transect inside the southern gyre	2004	This study*
	1964 (1003) D1S5N10			Eastern transition area	2004	This study*
	464 (305) D1S3N6			Chilean upwelling	2004	This study*

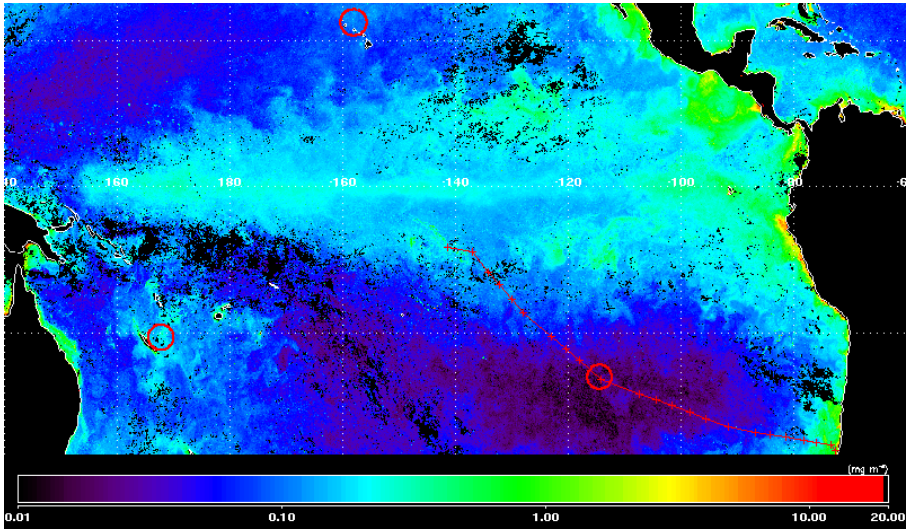

Fig. 1. Location of the stations sampled during the BIOSOPE cruise (November–December 2004) and of the three stations (red circle) where current P pools and availability are compared: a station in the centre of the South gyre (S-gyre station), ALOHA station frequently sampled since the 1980s (N-gyre station) and a station sampled during the DIAPALIS cruises (2001–2002) in the SW Pacific Ocean (SW station).

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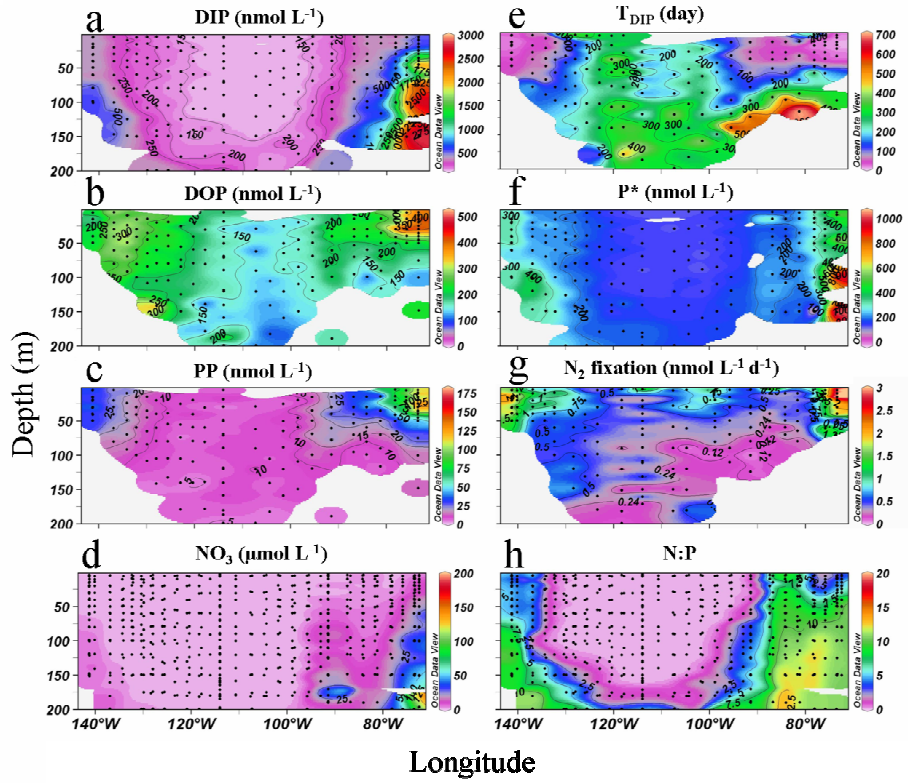

Fig. 2. (a) DIP, **(b)** DOP, **(c)** PP, **(d)** NO_3^-, **(e)** DIP turnover time, **(f)** P*, **(g)** N_2 fixation rates and **(h)** NO_3^-/DIP measured during the BIOSOPE cruise (November-December 2004) in the South Pacific between the Marquesas Islands and the Chilean coast. ODV (Schlitzer, 2002) was used to generate the distribution maps.

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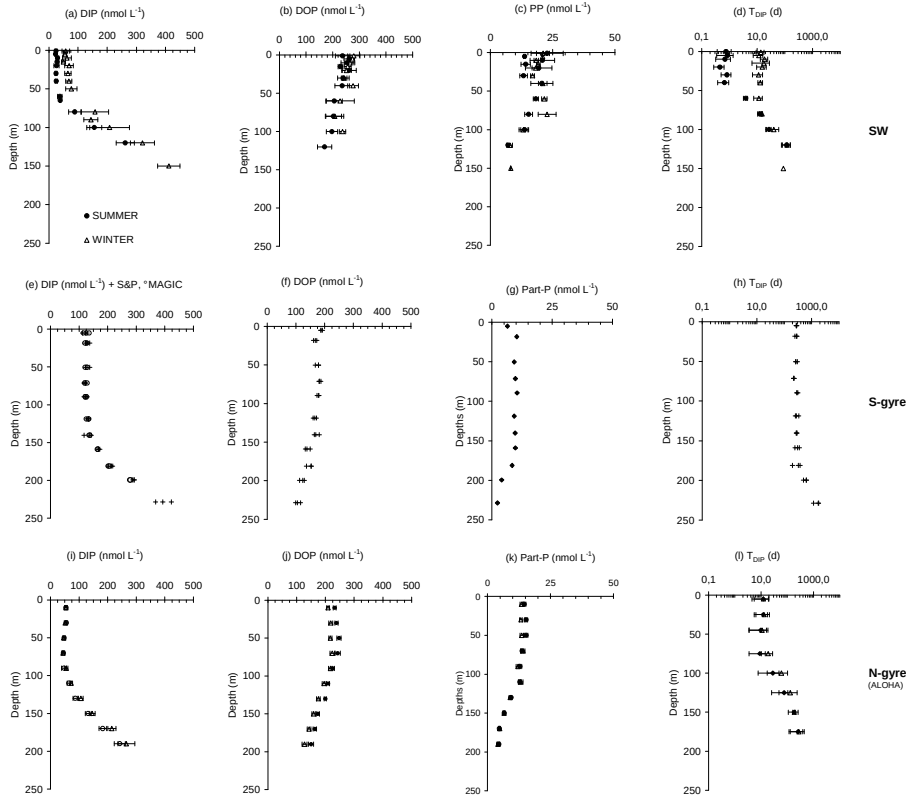

Fig. 3. Current Dissolved Inorganic P (DIP), Dissolved Organic P (DOP), Particulate P (PP) concentrations, and DIP turnover time vs. depth at the three stations studied in the South, North and Southwestern tropical Pacific Ocean. Summer and Winter concentrations are indicated when available.

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