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Carbon and nitrogen uptake in the South Pacific Ocean: evidence for efficient dinitrogen fixation and regenerated production leading to large accumulation of dissolved organic matter in nitrogen-depleted waters

P. Raimbault and N. Garcia

Laboratoire d'Océanographie et de Biogéochimie (UMR 6535 CNRS), Centre d'Océanologie de Marseille, Université de la Méditerranée, Campus de Luminy, 13288 Marseille Cx 09, France

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Correspondence to: P. Raimbault (patrick.raimbaulr@univmed.fr)

Abstract

A major goal of the BIOSOPE cruise on the R/V Atalante to the South Pacific Ocean (conducted in October–November 2004) was to establish rate of productivity along a longitudinal section across the oligotrophic South Pacific Gyre (SPG), and compared these measurements with those obtained in nutrient–repleted waters from Chilean upwelling and around Marquesas Islands. A dual $^{13}C/^{15}N$ isotopic technique was used to estimate rates of carbon fixation, inorganic nitrogen uptake (including dinitrogen fixation), ammonium (NH_4) and nitrate (NO_3) regeneration, and dissolved organic nitrogen (DON) release resulting from both NH_4 and NO_3 uptake. The SPG had revealed the lowest rates of primary production (0.1 $gC.m^{-2}.d^{-1}$), while rates were 7 to 20 fold higher around the Marquesas Islands and in the Chilean upwelling, respectively. In this very low productive area, most of primary production was sustained by active regeneration processes which fuelled up to 95% of the biological nitrogen demand. Since nitrification was very active in the surface layer and often balanced the biological demand of nitrate, dinitrogen fixation, although acting at low daily rate (≈1–2 nmoles $l^{-1}d^{-1}$), sustained the main part of new production. Then, new production in the SPG (0.008±0.007 gC $m^{-2}.d^{-1}$) was two orders of magnitude lower than this measured in the upwelling where it essentially sustained by nitrate (0.69±0.49 $gC.m^{-2}.d^{-1}$). In the whole investigated region, the percentage of nitrogen release as DON represented a large part of the inorganic nitrogen uptake (13–15% in average), and reaching 26–41 % in the SPG where the production of DON appeared to be a major part of the nitrogen cycle. Due to the lack of annual vertical mixing and very low lateral advection, the high release rates could explain the large accumulation of dissolved organic matter observed in the nitrogen-depleted and low productive waters of the South Pacific Gyre.

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1 Introduction

The nitrogen cycle in the oceanic gyres has been studied since the pioneering work begun by Menzel and Ryther in the Sargasso Sea (Menzel and Ryther, 1960; Ryther and Menzel, 1961). Some years later, Dugdale and Goering (1967) defined new and regenerated nitrogen and, hence new production, fuelling by allochthonous N-sources (mainly NO_3^-) supplied via diffusion from the nitracline. On the other hand, "regenerated" production is fuelled by autochthonous N-sources (mainly NH_4^+), derived from biological processes (Harrison et al., 1987). The fraction of primary production based on new nutrients is termed the *f*-ratio (Eppley and Peterson, 1979) and, at steady state, accounts for the proportion of production available for export. Historically, measurements of the nitrogen cycle were primarily based on ^{15}N tracer techniques. New production estimates, computed in terms of carbon by using the *f*-ratio and primary production, has known considerable variability (Aufdenkampe et al., 2002), due to the inaccuracy in estimating *f* and NO_3^- assimilation (Priscu and Downes, 1985; Ward et al., 1989; Gentilhomme and Raimbault, 1994; Raimbault et al., 1999; Diaz and Raimbault, 2000; Aufdenkampe et al., 2001).

Some of the main sources of error in classical ^{15}N uptake experiments are still being debated, like nitrogen regeneration and release of dissolved organic nitrogen (DON) which inspired several revisions of the concepts of new and regenerated production (Fernandez and Raimbault, 2007). Ammonium regeneration is the main source of regenerated nitrogen to the euphotic zone. By studying ammonium isotopic dilution (recycling of unlabeled substrate) during ^{15}N incubation experiments, Glibert et al. (1982), and Harrison et al. (1987) showed that ammonium regeneration can result in significant underestimations of regenerated production, which would also bias the assessment of the *f* ratio. Nitrification (the oxidation of NH_4 to NO_3 mediated by bacteria) is also an important variable, now not only considered responsible for the deep nitrate reservoir but also believed to provide a source of "in situ" regenerated nitrate at the base of the euphotic zone (where phytoplankton is light limited to compete for NH_4^+, see re-

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view in Ward 2000). Eppley et al. (1990) and Eppley and Koeve (1990) found rapid production of nitrate at shallow depth (20 m) in the Atlantic. Until the last decade, nitrification was thought to be restricted to specific environments but it is now known that it is more widely distributed (Zehr and Ward, 2002). Ward et al. (1989) and Eppley and Renger (1986) pointed out the importance of this process to new production in the southern California Bight. In the permanently oligotrophic North pacific Dore and Karl (1996) found nitrification could supply 47–142% of nitrate assimilation, results equivalent to those found in the equatorial Pacific, where nitrification can fuel 20 to 100% of new production (Raimbault et al., 1999). Its role in providing regenerated nitrate in the euphotic zone has been confirmed by recent findings in the Atlantic as well as in the Mediterranean Sea, where nitrification can support 25 to 100% of new production (Diaz and Raimbault, 2000; Fernandez and Raimbault, 2007). Failure in estimating dissolved inorganic nitrogen (DIN) taken up by phytoplankton and released as DON represents another and not entirely resolved source of error in DIN uptake rates (Bronk et al. 1994; Slawyk and Raimbault 1995). However, the impact of such processes is still rarely accounted as a possible overestimation factor in new production calculations and new production models suffers from a general lack of data, probably related to schedule constraints and the labour intensive nature of the methods involved. Finally, oceanographers have traditionally viewed the upward eddy-diffusive flux of nitrate as the nearly exclusive source of new nitrogen supporting the export flux of biogenic particles in the open oceans. In fact, the ubiquitous pool of dinitrogen gas (N_2) dissolved in the sea can represent a significant source of new nitrogen and estimates of biological nitrogen fixation have been recently revised upward (Galloway et al., 1995; Grüber and Sarmiento, 1997; Capone and Carpenter, 1999). In the north subtropical and tropical Atlantic and Pacific oceans, it has been estimated that N_2fixation is equivalent to 50–180% of the flux of nitrate into the photic zone (Capone et al., 2005), demonstrating that a large part of new primary production is fuelled by N_2fixation rather than deep nitrate diffusing from deeper layer into the photic zone. While the large size classes (*Trichodesmium* and diatoms containing endosynbiotic *Richelia*) are thought to be re-

sponsible for the vas majority of N_2 fixation, recent works pointed out the important contribution of nanoplanktonic N_2-fixers (Zehr et al., 2001; Karl et al., 2002). These small diazotrophic organisms, while present at low cellular concentration, could sustain a great part of the new production under nitrate-depleted conditions (Montoya et al., 2004; Falcon et al., 2002; Garcia et al., 2006, 2007). By representing 60% of the global ocean's area, the subtropical open-ocean ecosystems are the largest coherent biomes of our planet and the biogeochemical processes they support have global consequences (Karl, 2002). These environments provide ideal ecological niche for the development of nitrogen-fixing organisms. However, all of the studies dedicated to the nutrient control of nitrogen fixation have concentrated so far on the northern hemisphere and there is extremely few data available on the southern hemisphere, which contains the largest ocean area of the global ocean. Thus, precise measurements of nitrogen utilization are crucial to correctly relating new production to export of particulate (Eppley and Peterson, 1979) and dissolved (Toggeweiler, 1989) organic matter to deep ocean, and to quantify the biological impact of the ocean on the global carbon cycle. At present, however, the magnitude of these key fluxes is under debate, especially in oligotrophic waters, which represent a great fraction of the global ocean. As our understanding of the nitrogen cycle recently moves on, these facts lead to a new revision of the *f* ratio and to important implications for the annual budget of the carbon and nitrogen cycles. Methods are now available to investigate simultaneously in oligotrophic waters primary production, nitrogen uptake including dinitrogen fixation (Montoya et al., 1999) and nitrogen regeneration (Glibert et al., 1982; Raimbault et al., 1999), as well as organic matter release (Bronk and Glibert, 1995; Slawyk and Raimbault, 1995; Karl et al., 1998). In this context, the BIOSOPE (BIOgeochemistry and Optics South Pacific Experiment) cruise was scheduled to provide a complete data set of biogeochemical parameters in the South Pacific Ocean. The South Pacific Central Gyre has been described as the most oligotrophic zone in the world ocean (Claustre and Maritorena, 2003) with an extreme nutrient limitation. It is also one of the least studied areas of the Ocean (Daneri and Quinones, 2001). The 8000 km transect,

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stretching from the Marquesas Islands to the Chilean coast and crossing the centre of South Pacific Gyre, is an ideal area to study primary production and new production along an extreme trophic gradient. The present work focuses on the geographical distribution of photosynthetic carbon fixation, nitrogen assimilation (including dinitrogen fixation and release of dissolved organic nitrogen) and nitrogen regeneration in order to accurately estimate primary production and *f* ratio, e.g. the fraction sustained by "new" nitrogen. Additionally, it provides an objective methodological approach to the difficulty of estimating new production in oligotrophic systems.

2 Methods

This work was carried out on board the R/V Atalante in October-November 2004. Data were gathered during the BIOSOPE (BIOgeochemistry and Optics South Pacific experiment) cruise carried out in the southeast Pacific Ocean along a transect stretching from the Marquesas archipelago to the Chilean coasts (between 146.36 W and 72.49° W, Fig. 1).

Twenty four short stations have been sampled along a 8000 km transect crossing different oceanic situations. The mesotrophic area associated to the plume of the Marquesas Island (141° W–134° W), the adjacent high nitrate – low chlorophyll waters (132°–123° W), the ultra-oligotrophic waters associated with the central part of the south pacific gyre (123° W–101° W), the oligotrophic eastern side of the gyre (101° W–81° W) and the Chilean upwelling (80° W–72° W). In addition, six experimental sites were specifically investigated with long fixed stations (over 2–5 days), representing different trophic regimes sites : MAR=Marquesas archipelago (141,3° W; 8.4° S); HLN = High Nutrient Low Chlorophyll area east of the Marquesas islands (136.8° W; 9° S); GYR = centre of the South pacific gyre 114° W, 26° S); EGY = eastern border of the gyre (91.4° W, 31.8° S), UPW and UPX situated in the area of Chilean upwelling (73° W–34° S and 72.4° W–34.5° S). Station from the gyre has been selected from ocean color images as having the lowest surface chlorophyll concentration in the world ocean.

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Nutrient measurements were performed at every station of the grid. For nitrate and nitrite determination, samples were taken in 250 ml polyethylene flasks and analyzed on board immediately after sampling using a semi automatic Technicon Autonanalyser® II according to Raimbault et al. (1990) for low-nitrate water (<500 nmoles.l^{-1}; detection limit=3 nmoles.l^{-1}) and Tréguer and Lecorre (1975) for high-nitrate water (>500 nmoles.l^{-1}; detection limit=0.05 μmoles l^{-1}). Ammonium concentrations (40 ml collected in 50 ml Schott glass bottle) were measured using the fluorometric method (Holmes et al., 1999; detection limit=0.005 μmoles l^{-1}).

At each production station, rates of carbon fixation (primary production), nitrate and ammonium uptake as well dinitrogen fixation (diazotrophy) were measured by using a dual $^{13}C/^{15}N$ isotopic technique. For this purpose, three 580 ml samples were collected before sunrise at 6–7 standard depths between the surface and 1% light, and poured into acid-cleaned polycarbonate flasks. Bottles were rinsed after use with 10% HCl, then with distilled water from a Milli Q ion exchange unit.

In each bottle, bicarbonate sodium ^{13}C labelled ($NaH^{13}CO_3$ – 6 g 250 ml^{-1} deionized water –99 at % ^{13}C, EURISOTOP) was added in order to obtain ≈10% final enrichment (0.5 ml 580 ml^{-1} sea water). Then, the $^{15}N_2$ gas (99 at % ^{15}N, EURISOTOP) was introduced to bottles equipped with a gas-tight septum (2 ml of gas 580 ml^{-1} sea water). We added a fixed quantity of $^{15}N_2$ gas and calculated the enrichment of each bottle on the basis of its volume and the solubility of N_2. We used the equations provided by Weiss (1970) to calculate the N_2 initial concentration, assuming equilibrium with the overlying atmosphere. The $^{15}N_2$ enrichment in the incubation bottles ranged between 22% and 25%, for seawater temperature varying from 15°C (in the upwelling) to 27°C (in the subequatorial zone). The sample was carefully shaken to allow rapid equilibration between $^{15}N_2$ and natural N_2.

Nitrogen ^{15}N-tracer additions as $K^{15}NO_3$ or $^{15}NH_4Cl$ (99% at ^{15}N) were usually 10%–20% of the ambient concentration based on real-time measurements. In nutrient impoverished waters, when concentrations were lower than the detection limit, additions of ^{15}N were fixed to ~17 nmoles l^{-1} for ^{15}N-NO_3 and 43 nmoles l^{-1} for ^{15}N-NH_4.

Incubations were started immediately after tracer addition just before dawn. They were done on-deck in an incubator, which consisted of 6–7 opaque boxes, each with a light screen that allowed 50%, 25%, 15%, 8%, 4%, 1% and 0.3% of light penetration. The incubator was maintained at sea-surface temperature with pumped sea water. During the 5 experimental sites, incubations were performed in situ on a drifting rig at the same depth from which they were collected. After 24 h (dawn to dawn), final concentrations of NO_3^- and NH_4^+ were measured and samples were filtered thereafter on precombusted (450°C) Whatman GF/F filters (25 mm in diameter) using a low vacuum pressure (<100 mm Hg). At the same time, filtrates from ^{15}N-NH_4 experiments were recovered in Duran Schott flask and poisoned with 1 ml $HgCl_2$ (6 g l^{-1}) in order to prevent bacterial activity during conservation. An aliquot of these filtrates (200 ml) was filtrated again on 0.2 μm Teflon membrane. Filtrates from ^{15}N-nitrate flasks were collected during in situ experiments, only. In this case 300 ml of < GF/F filtrate were refiltrated through 0.2 μm Teflon membrane and stored as indicated above. After filtration, filters were placed in pre-combusted glass tubes, dried during 24 h in a 60°C oven and stored dried until laboratory analysis. These filters were used to determine the final ^{15}N /^{13}C enrichment in the particulate organic matter as well as concentrations of particulate carbon and particulate nitrogen.

The dual isotopic enrichment analysis were performed on a Integra-CN mass spectrometer calibrated with glycin references every batch of 10–15 samples. The accuracy of our analytical system was also regularly verified using reference materials from the International Atomic Energy Agency (AIEA, Analytical Quality Control Services). The mean atom% ^{15}N does not vary between 0.2 and 10 μmoles N. Then, the low background of the system allows to analyse safely samples containing low nitrogen concentrations (0.4–1 μmole), values often observed in surface oligotrophic waters. The ^{15}N isotope enrichment of a sample is reported in term of atom % excess ^{15}N overtime, that refers over the atom% ^{15}N in no-enriched sample issued from the same phytoplankton population. Therefore, value of time zero enrichment is necessary and determined with samples (same volume as incubated sample) which are filtered im-

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mediately after isotope addition. For N_2 experiments, time zero value, established with 8 samples, was 0.3676±0.007%. For $^{15}N\text{-}NO_3$ and $^{15}N\text{-}NH_4$experiments, time 0 enrichment was 0.372±0.007%. We considered as significant, results with ^{15}N excess enrichments higher than 0.014 % (two times the standard deviation obtained with time zero samples).

The transport rate of ^{15}N-labelled dissolved inorganic nitrogen (DIN), from the DIN pool to the PON pool, i.e., the net DIN uptake (ρ^{net}_{DIN} in nmoles l^{-1} d^{-1}) was computed, according to Dugdale and Wilkerson (1986), from Eq. (1):

$$\rho^{net}_{DIN} = \frac{R_{PON}}{R_{DIN} \times T} \times [PON] \quad (1)$$

Where R_{PON} and R_{DIN} represent the ^{15}N atom % excess enrichment in the PON and DIN pools respectively, [PON] represents the final PON concentration and T represents the incubation period (in day). As mentioned after, to correct ammonium uptake rates for isotopic dilution, we made R_{DIN} in Eq. (1) equal to the mean value between initial and final R_{NH_4}. According to these experimental conditions, the detection limit for nitrogen uptake, calculated from significant enrichment (0.014% in excess) and lowest particulate nitrogen (0.2 μmole N) is estimated from Eq. (1) to 0.12 nmol.l^{-1}.d^{-1} for nitrogen-fixation (mean $R_{DIN} \approx 24\%$) and 0.03 nmol.l^{-1}.d^{-1} for nitrate and ammonium uptake in nutrient-depleted waters ($R_{DIN} \approx 100\%$).

Carbon fixation rates were calculated according to Slawyk and Collos (1984), with a time 0 enrichment of 1.113±0.005% (n=8). This time 0 value is little higher than the natural abundance for phytoplankton (1.089), certainly due to some residual traces of ^{13}C tracer. It should be noted that ^{13}C enrichment of samples was less problematic than ^{15}N enrichment, since inorganic carbon is assimilated by the whole phytoplankton, and excess values ranged from 0.3 to 3.6%. Data of ^{13}C fixation rates, e.g. primary production, corresponding to the mean of the three replicates, are expressed in μgC l^{-1} d^{-1}. Applying similar calculation than for nitrogen, the detection is limit is estimated to 0.35 μg C.l^{-1}.d^{-1}.

Filtrates <GF/F from $^{15}NH_4$ incubations were used to measure the final ^{15}N enrichment 1) in the DIN pool and 2) in the <GF/F organic matter pool, as outlined by Raimbault et al. (1999). In this procedure, all forms of DIN are removed from the sample as $(NH_4)_2SO_4$, by successive diffusion and reduction processes. The first diffusion step allows to quantify the final ^{15}N enrichment of the ammonium pool, and to estimate isotope dilution of the tracer due to NH_4 regeneration. During the second diffusion, the ^{15}N enrichment of the nitrate pool in the ammonium filtrates allows to quantify the oxidation of ammonium to nitrate (nitrification). During the third diffusion, the ^{15}N enrichment was determined in the <GF/F fraction to estimate the rate of ^{15}N-NH_4 accumulation in the <GF/F organic matter (dissolved organic nitrogen + <GF/F particulate nitrogen). The <0.2 μm filtrates from ^{15}N-NH_4 and ^{15}N-NO_3 experiments were used to measure ^{15}N enrichment in the <0.2 μm, fraction which only contents dissolved organic nitrogen (DON), e.g. to estimate loss of tracer in term of DON (ρ^{loss}_{DIN}).

Ammonium regeneration rates (rNH_4 in nmoles.l^{-1}.d^{-1}) were estimated according to Laws (1984):

$$NH_4 = \frac{[NH_4]_I + [NH_4]_F}{2 * T} * \mathrm{Ln}\left(\frac{Ro_{NH_4}}{Rf_{NH_4}}\right) \quad (2)$$

Where $[NH_4]_I$ and $[NH_4]_F$ represent initial and final concentrations of ammonium during the incubation experiment. Ro_{NH4} and Rf_{NH4} are the initial and final excess enrichments in ^{15}N-NH_4 for the incubation period.

Nitrification rates (ρ_{NIT} in nmoles.l^{-1}.d^{-1}) were computed according to Raimbault et al. (1999):

$$\rho_{NIT} = \frac{R_{NO_3}}{R_{NH_4} \times T} \times [NO_3] \quad (3)$$

Where R_{NO_3} is the ^{15}N atom% excess enrichment in the $(NO_3^- + NO_2^-)$ pool,R_{NH_4} is the mean ^{15}N atom% excess enrichment of the NH_4^+ pool, and $[NO_3]$ is the final NO_3^-

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concentration in the filtrate.

The measurement of ^{15}N abundance in organic matter less than GF/F ($R_{<GF/F}$) allowed us to calculate the ammonium uptake in the <GF/F fraction ($\rho_{NH_4}^{<GF/F}$), calculated as following (Eq. 4):

$$\rho_{NH_4}^{<GF/F} = \frac{R_{<GF/F}}{R_{NH_4} \times T} \times [PON_{<GF/F}] \quad (4)$$

Where $R_{<GF/F}$ and R_{NH_4} are the ^{15}N atom % excess enrichment of the <GF/F fraction and final ammonium pool respectively, and $[PON_{<GF/F}]$ is the final particulate nitrogen less than GF/F. The measurement of ^{15}N abundance in the extracelullar DON pool (R_{DON}) allowed us to calculate the DIN (nitrate or ammonium) lost (ρ_{DIN}^{loss}) as DON (Eq. 5), calculated as outlined by Slawyk et al. (1998):

$$\rho_{DIN}^{loss} = \frac{R_{DON}}{R_{DIN} \times T} \times [DON] \quad (5)$$

Where R_{DON} and R_{DIN} are the ^{15}N atom % excess enrichment of the extracellular DON and DIN pool respectively, and [DON] is the final extracellular DON concentration. The quantification of the ρ_{DIN}^{loss} offers the possibility to calculate the gross uptake rate ρ_{DIN}^{loss} as the sum of the net DIN uptake and the DIN loss:

$$\rho_{DIN}^{gross} = \rho_{DIN}^{net} + \rho_{DIN}^{loss}$$

During our study, nitrate and ammonium concentrations were often lower the detection limit (especially in the South Pacific Gyre) and it was experimentally impossible to reduce the tracer addition to the ideal level (<10% of ambient concentration). In this nutrient conditions, addition of tracer would violate the general assumption that addition of tracers does not disturb the steady-state of the system and may have involved a major perturbation of the nitrate and ammonium uptake (Allen et al., 1996; Harrison et al., 1996). But the use of kinetics parameters described by Harrison et al. (1996)

allowed us to account for uptake rate enhancement according to the following equation given by Rees et al. (1999),

$$\rho N_H = \rho N_0 / [N_{sp}/(Ks + N_{sp}) \times (Ks + N_A)/N_A] \quad (6)$$

Where N is nitrate or ammonium, ρN_0 is the original uptake rate (nmoles l^{-1} d^{-1}), ρN_H is the uptake rate adjusted for enhancement of tracer, N_{sp} is ambient + tracer nutrient (nmoles), N_A is the ambient nutrient and Ks is the half-saturation constant. In this case, N_A was assumed to be 3 nmoles l^{-1} for nitrate and 5 nmoles l^{-1} for ammonium, corresponding to the detection limit of our analytical procedures. To quantify the affinity constant Ks, two kinetic studies were performed with 6 graduate additions of ^{15}N-labeled substrate (Fig. 2). Monod equation [V=Vm.S/(Ks+S)] was assumed, where V is the uptake rate for substrate concentration S, Vm is the saturated uptake rate and K_S, the affinity constant, e.g. the substrate concentration at half Vm. The kinetics constant K_S, needed for the use of Rees et al.'s model, was derived from the Wolf plot linear transformation of S/V vs S. Ks obtained during the 4 experiments performed in nitrogen-depleted waters (12.9 and 15 nmoles.l^{-1} for nitrate and ammonium, respectively) were a little lower than those in other oceanic waters (around 25–30 nmoles.l^{-1}) by Sahlsten (1987) and Harrison et al. (1996). In first approximation, we assumed that DIN losses as DON (ρ_{DIN}^{loss}) and nitrification (ρ_{NIT}) could be activated in the same way as net uptake rates, and we applied to theses processes the same procedure of correction.

More, spiked nutrients additions in nutrient-poor waters could be also stimulated ^{13}C fixation. Then samples enriched with ^{15}N-N_2, that no significantly change N_2 concentration in samples, were used to test the absence of interference on primary production caused by ^{15}N-tracer additions in oligotrophic waters (Fig. 3). The model II gives a regression coefficient of 0.98, revealing no significant stimulation of primary production by low nutrient addition, at least during the 24 h experiments. Since ^{13}C isotope is not still currently used for estimating marine productivity, especially in oligotrophic oceanic area, our results ($PP^{13}C$) also offer the opportunity to perform an extensive comparison

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with classical primary production measurements conducted with ^{14}C tracer ($PP^{14}C$) in the same conditions (T. Moutin, personal communication). Pooling all data obtained during in situ experiments and using the model II linear regression, we note any significant deviation ($PP^{13}C = 1.02\,PP^{14}C + 0.14$, $r^2 = 0.98$; n = 50), indicating the good efficiency of the ^{13}C procedure to quantify the photosynthetic carbon fixation in oligotrophic waters.

The depth of the euphotic zone (Ze), representing the depth where the irradiance is reduced to 1% of its surface value, was computed using the in situ TChl*a* concentration profiles (see Ras et al., 2007) according the model developed by Morel and Maritorena (2001). Data throughout this paper are limited to the 0–200 m water column.

3 Results

A detailed description of the geographical distribution of nutrients and biomass during this study can be found in companion paper (Raimbault et al., 2007). Briefly, longitudinal distribution of surface nitrate showed minimal values (lower than the detection limit of 3 nmoles. l^{-1}) between 125° W and 95° W, e.g. in the South Pacific gyre (SPG) . Other studied regions (Marquesas Islands and Chilean upwelling) showed significant nitrate concentrations (>0.5 μmoles.l^{-1}) in surface. Chlorophyll biomass followed this general trend with very low values in the center of the SPG (0.023 $\mu g.l^{-1}$) while levels reached 0.3 $\mu g\,l^{-1}$ and 1 $\mu g\,l^{-1}$ near the Marquesas Islands and in the Chilean upwelling, respectively. The photic layer located around 40–50 m in the Marquesas and upwelling regions deepened in the centre of the SPG, reaching 160 m between 120° W and 105° W, in the clearest natural water in the world (Morel et al., 2007). The incident solar radiation was more or less constant during the cruise (41± 7 $Em^{-2}\,s^{-1}$) except during three very cloudy days (9 to 11 November 2004, e.g. from 120° W to 117° W) where incident radiation strongly decreased to 14–20 $Em^{-2}\,s^{-1}$ (H. Claustre, personal communication).

Primary production and nitrogen uptake rates described the same general distribution, responding to nutrient variation observed in the photic layer along the transect (Fig. 4). A large central area was characterized by very low rates surrounded with two small regions: the subequatorial Marquesas region (in the west) where primary production reached 10 μg C l^{-1} d^{-1} in surface, and a part of the Chilean upwelling in the east, which was the most productive area with primary production higher than 50 μgC $l^{-1}d^{-1}$. The most part of the transect (e.g. the South Pacific Gyre = SPG) was characterized by very low carbon fixation rates, less than 2 μg C l^{-1} d^{-1} between 130 and 95° W. It would be noted that in this centre of the SPG, vertical variations of primary production were very weak, rates remaining more or less constant (≈1–2 μg C l^{-1} d^{-1}) between the surface and the base of the photic layer. Nitrate and ammonium uptake rates followed the same general pattern than primary production. Nitrate uptake ranged between 100–500 nmoles l^{-1} d^{-1} in the upwelling and less than 5 nmoles l^{-1} d^{-1} in the SPG. Intermediate values were found near the Marquesas Islands ranging between 20 and 100 nmoles l^{-1} d^{-1}. Ammonium uptake rates (corrected from isotopic dilution) were always significantly higher than nitrate uptake rates. Upwelling presented again the highest uptake rates (up to 500 nmoles l^{-1} d^{-1}), Marquesas Island the intermediate levels (up to 100 nmoles.l^{-1} d^{-1}), and SPG very low rates (<40 nmoles.l^{-1} d^{-1}). As for primary production, vertical distribution of ammonium uptake, as well as nitrate uptake were quite homogeneous in the SPG, with very low vertical variation and any clear surface or subsurface maximum. But, it would be noted, that contrary to primary production, noticeable rates of ammonium and nitrate uptake (>60 and > 5 nmoles l^{-1} d^{-1}, respectively) were detected until 100 m on the eastern edge of the SPG between 90 and 100° W.

Dinitrogen fixation rates showed a particular distribution, with rates always lower than ammonium and nitrate uptake. First, vertical extension of this biological process was more important in the west part (until 150 m) than in the eastern part of the investigated area. Second, nitrogen fixation was essentially located near the surface in the SPG where a clear surface maximum can be detected. Rates decreased rapidly with depth

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and were <0.5 nmoles l^{-1} d^{-1} below 50 m. The geographical gradient was weak since maximum surface rates measured in the upwelling (3.6 nmoles.l^{-1} d^{-1}) was only two fold higher than the maximum rates measured in the SPG (1.8 nmoles.l^{-1} d^{-1}). The Marquesas Island was marked by intermediate nitrogen fixation (≈2 nmoles.l^{-1} d^{-1}).

Ammonium regeneration rates showed the same regional variations. This process was very active in surface water near the upwelling (>200 nmoles.l^{-1}.d^{-1}), as well as around the Marquesas Islands with rates >100 nmoles.l^{-1}.d^{-1} until 135° W. Surface values decreased to 20 nmoles.l^{-1}.d^{-1}in the SPG, but these rates remained more or less constant between surface and 200 m depth. As for ammonium uptake, a subsurface maximum (125 m) was detected around 90° W on the east edge of the SPG. The significant ammonium regeneration measured at all stations, whatever the trophic level, induced great variations of ammonium enrichment during the 24 h incubations. The Fig. 5 demonstrated that no taking into account isotopic dilution leads to strong underestimation of ammonium uptake always higher than 50%. More, any relationship was found between the magnitude of underestimation and the uptake rates, clearly indicating that estimations of isotopic dilution are absolutely required to correctly quantify ammonium uptake during 24 h incubation, even in oligotrophic waters.

Nitrification showed similar pattern than ammonium regeneration indicated a tight coupling between the two processes although rates, always significant, were globally one order of magnitude lower than those of ammonium regeneration. Highest nitrification rates (>30 nmoles l^{-1} d^{-1}) were observed in the upwelling with a westward extension until 90° W. The subsurface patch of ammonium regeneration at 90° W was also marked by active nitrification (up to 40 nmoles l^{-1} d^{-1}). Marquesas region was characterized by relatively low nitrification rates (5–10 nmoles l^{-1} d^{-1}), while lowest but detectable values (<5 nmoles l^{-1} d^{-1}) were measured in the SPG. As observed for preceding biological processes, nitrification was again homogeneous over the water column without any significant maximum in the oligotrophic central region. Nitrate uptake compared to nitrification generally dominated in the upper layer. At the base of the photic layer, nitrification rates were 2 to 10 times higher than corresponding nitrate up-

take rates, especially in the upwelling area. However, both rates were quite similar over the photic layer in the SPG.

A significant part of ammonium was assimilated in the fraction less than GF/F (Fig. 6). This <GF/F ammonium uptake was large in the upwelling region, with rates higher than 25 nmoles.l^{-1} d^{-1} and up to 170 nmoles l^{-1} d^{-1}, but also obviously significant in the SPG (10 to 20 nmoles l^{-1} d^{-1}). A part of this <GF/F uptake was ultimately found in the <0.2 μm fraction, e.g. in the dissolved organic nitrogen pool, rates here named as ρ_{loss}. Ammonium loss in term of DON was again highest in the upwelling area (50 to 100 nmoles l^{-1} d^{-1}), but highly significant in the oligotrophic SPG (5 to 20 nmoles l^{-1} d^{-1}). The lowest rates (<5 nmoles l^{-1} d^{-1}) were measured in the west part of the section. The nitrate loss was lowest in the SPG (1 to 5 nmoles l^{-1} d^{-1}) and highest in the surface waters of the upwelling (100 nmoles l^{-1} d^{-1}). Some data in the SPG appeared close to zero, which may partly explained by the very low uptake rate and very low excess enrichment in the <0.2 μm DON pool (close to 0.01%). Loss of nitrate tended generally to rapidly decrease with depth as observed in the most productive region (Marquesas Islands and Chilean upwelling). The mean percentages of DIN loss showed important regional variations (Table 1). The lowest productive system (SPG) revealed the most important loss of recently nitrogen uptake (>20%), while in the other regions percentages were lower than 15%. It would be noted that percentages of N-nitrate loss were generally equivalent to those of N-ammonium loss, except around the Marquesas Islands (Mar and HLN sites).

Concerning the *f* ratio, several corrections have been applied to take into account of several processes rarely measured during nitrogen uptake experiments, as nitrification, DIN loss and nitrogen fixation. Nitrification (as a source of nitrate) can induce overestimations of new production by adding to the nitrate pool some NO_3^- coming from what is, actually, regenerated production (Dore and Karl 1996; Ward et al. 1989; Priscu and Downes 1985; Dugdale and Goering 1967). Then, the fraction of nitrate that was produced by nitrification (ρ_{NIT})was subtracted from total nitrate uptake (ρ_{NO_3}) in order to truly assess the uptake of "new" nitrate as classically defined by Dugdale

and Goering (1967). As nitrogen fixation rates (ρ_{N_2}) were available, they were included in calculation of new production (Pnew), calculated as following:

$$\text{Pnew} = \rho_{N_2} + (\rho_{NO_3} - \rho_{NIT}). \quad (7)$$

When nitrification rates were higher than nitrate uptake ($\rho_{NO_3} - \rho_{NIT<0}$), Pnew is estimated to be equal to ρ_{N_2}. According to this assumption, the f ratio can be calculated as followed:

$$f = \frac{\rho_{N_2} + \rho_{(NO_3^-)} - \rho_{NIT}}{[\rho_{N_2} + \rho_{(NO_3^-)} + \rho_{(NH_4^+)}]} \quad (8)$$

As ρ_{loss} were not available for all stations (especially from ^{15}N-NO_3 experiments), gross uptake rates were not used for the calculation of the f ratio, which was estimated with the net uptake rates. Using data coming from in situ experiments during which both losses of N-nitrate and N-ammonium were measured, the model regression analysis (Sokal and Rohlf, 1995) gives a slope of 1.02 (Fig. 7). The slope was not significantly different from 1, indicating that inclusion of DIN loss does not change estimations of f ratios. To assess the influence of nitrification and N_2-fixation in the magnitude of f ratio, we compare the f ratio calculating according Eq. (8) to those calculated without nitrification (f_{-NIT}) or without N_2-fixation (f_{-N_2}). The possible over-estimation due to the non inclusion of uptake of urea could not be evaluated, since flux of this organic nitrogen compound has not been investigated in this area.

The geographical variations of the different calculated f ratios (averaged over the photic layer) appear closely related to the distribution of the levels of primary productivity (Fig. 8), with highest values (>0.30) observed in the upwelling. Waters surrounding the Marquesas Islands were characterized by f ratio ranged between 0.1 and 0.2. In the SPG, f ratio was generally lower than 0.1, with very low values (0.02) found in the centre. The no inclusion of nitrification rates (f_{-NIT}) significantly increased f values in the SPG (0.08–0.15). In the other regions nitrification, although acting at significant rates, does not really modify mean f ratio. In the same manner, influence of nitrogen

fixation was only sensitive in the SPG. In this oligotrophic area, f_{-N_2} down to very low values (often close to 0) clearly indicating that nitrogen fixation was the main process providing new nitrogen in this upper layer.

4 Discussion

This study confirms previous satellite observation suggesting very low productivity in the SPG, e.g. in the clearest waters of the world ocean (Morel et al., 2007). Primary productivity (0.10 $gC.m^{-2}.d^{-1}$, Table 2) as well as new production (0.008 $gC.m^{-2}.d^{-1}$, Table 3) were the lowest rates ever measured in the ocean and can be considered as an end point for trophic level. Nixon (1995) assigned to oligotrophic, mesotrophic and eutrophic areas, annual carbon rates of <100, 100 to 300 and 300 to 500 g $C.m^{-2}.y^{-1}$, respectively. Following this criteria, and assuming that our measured rates remained constant over the year, Marquesas region appeared as mesotrophic (270 g $C.m^{-2}.y^{-1}$), upwelling (660 g $C.m^{-2}.y^{-1}$) as eutrophic and the SPG (36 g $C.m^{-2}.y^{-1}$) as an "ultra" oligotrophic system.

The longitudinal variation of integrated rates over the euphotic layer, using the trapezoidal method, revealed some specific patterns (Table 2). For example, enhancement of primary production and nitrogen uptake was not as pronounced as enhancement of nutrient availability. Although integrated nitrate concentration increased by a factor of 100 and 300 from the oligotrophic zone (0.9 $mmoles.m^{-2}$) to the Marquesas or to upwelling regions (128 $mmoles.m^{-2}$ and up to 285 $mmoles.m^{-2}$, respectively), integrated carbon fixation rates increased only by 10 to 20 fold. Nitrogen fixation appeared more or less constant around 0.03–0.11 $mmoles.m^{-2}.d^{-1}$, while integrated nitrate uptake increased 10 or 50 fold between the SPG (0.2 $mmoles.m^{-2}.d^{-1}$) in the Marquesas region (2.9 $mmoles.m^{-2}.d^{-1}$) or the upwelling (11 $mmoles.m^{-2}.d^{-1}$). The C/N uptake ratios were always lower than the conventional 6.6 Redfield ratio (Table 2). Such low C/N uptake ratio may suggest that some nitrogen assimilation (especially ammonium) was due to heterotrophic organisms. The large ammonium uptake measured in the

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<GF/F fraction (Table 1) seems to confirm this hypothesis. Assuming a C/N uptake by photosynthetic organisms close to 6.6, we can estimate the heterotrophic uptake rates of ammonium in the >GF/F fraction ($\Sigma H\rho_{NH_4}$). Except in the subequatorial site (MAR), this heterotrophic ammonium uptake could represent a large percentage (≈50%) of the gross ammonium uptake, which reached 70% in the SPG (Table 2). The importance of submicron heterotrophic organisms was here emphasized by the large amount of $^{15}N\text{-}NH_4$ ultimately found after 24 h incubation in the <GF/F fraction (Table 1). The low efficiency of GF/F filters for PON retention compared to 0.2 μm membranes is now well-documented in a variety of marine environments (Altabet, 1990; Libby and Wheeler, 1994; Slawyk and Raimbault, 1995; Raimbault et al., 2000; Fernandez et al., 2007) and has been confirmed during this study (Raimbault et al., 2007). Our experiments showed that the use of GF/F filters can result in severe underestimations of ammonium uptake under high productivity as well as under oligotrophic conditions. This possibility points out to a re-opening of the methodological debate on the use of GF/F and 0.2 μm filters for tracer addition experiments. But, since GF/F filters are able to correctly collect all particles containing chlorophyll, e.g. photosynthetic organisms (Chavez et al., 1995; Raimbault et al., 2007), this heterotrophic ammonium uptake has not to be included in the estimates of regenerated primary production. Consequently, the underestimation of gross ammonium uptake rates by filtration through GF/F filters should not have any consequences for *f* ratio estimation. Present data give no information on the possible nitrate uptake by the <GF/F fraction, but previous study in the Equatorial Pacific has shown that submicron particles passing through GF/F filters does not assimilate nitrate (Raimbault et al., 2000).

Due to the deviation of our C/N uptake relative to the Redfield ratio, there is not a good agreement between new production estimates obtained either from ^{13}C fixation rates multiplied by the independently calculated *f*-ratio or computed from direct measurements of new nitrogen multiplied by the 6.6 Redfield ratio (Table 3). The two estimates often disagree by 25–50%, with lowest (0.007–0.008 g $C.m^{-2}.d^{-1}$) and highest (0.53–0.69 g $C.m^{-2}.d^{-1}$) values found in the SPG and in the upwelling, respectively.

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The extremely low *f* ratio obtained in the SPG (0.05±0.03) confirms that the most entirely primary production, which maintained relatively significant rates over the 0–180 m water, was supported by regenerated nitrogen. This is indicated by the relatively high values of ammonium uptake (2.1 mmoles.m^{-2}.d^{-1}) as well as by significant ammonium and nitrate regeneration rates, 3.5 and 0.76 mmoles.m^{-2}.d^{-1}, respectively (Table 2). There are seldom measurements of NH_4 regeneration in the literature for oceanic waters but our results are in the range of the scarce available data (e.g. Bode et al. 2002; Raimbault et al., 1999; Fernandez and Raimbault, 2007). Ammonium regeneration showed high rates (up to 500 nmoles.l^{-1}.d^{-1}) in the high productive Marquesas and upwelling regions (MAR and UPW), but significant activity was also measured in the SPG (10–20 nmoles.l^{-1}.d^{-1}), rates sufficient to sustain the biological demand. This observation was confirmed by the picoplankton abundance which was strongly dominated by heterotrophic bacterioplankton along the whole transect (Grob et al., 2007).

Another important finding deals with the magnitude of the nitrification process in the euphotic layer. Although the potential significance of "regenerated" nitrate in the euphotic zone has been acknowledged for some time (Dugdale and Goering, 1967; Ward et al. 1989; Dore and Karl, 1996) and nitrification studies have been performed in a variety of marine environments (Ward et al., 1984, Codispoti and Christensen, 1985, Ward and Zafiriou, 1988), observations in the open ocean are rare. Nitrification rates presented here (Table 2) are in the range of previous observations (e.g. Ward and Zafiriou, 1988; Bianchi et al., 1994; Raimbault et al., 1999; Fernandez and Raimbault, 2007). Regeneration processes were active in the entire water column even in the oligotrophic waters of the SPG, and were largely able to sustain phytoplanktonic demand of nitrate in the photic layer (Table 2). Rates measured in the top 100 m suggest that about 80 to 100% of nitrate uptake in surface waters was supported by nitrification in the SPG. This result confirms the widely significant role of nitrification in the upper layers of oceanic waters, as previously found in the equatorial Pacific where 20 to 100% of total nitrate demand can be fueled by nitrification (Raimbault et al., 1999) and 142% at station ALOHA (Dore and Karl, 1996). A logical conclusion is the possibility of consid-

erable overestimations in current new production estimates if all nitrogen regeneration processes are not taken into account. In terms of integrated values over the photic layer, overestimation was only significant in the SPG, where rates of new nitrate assimilation (Pnew) were lower than expected, even close to zero. Consequently average values of *f* ratio was very low in the SPG and no zero values were essentially due to new production sustained by N_2–fixation, only source of new nitrogen in the upper layer of the SPG.

Nowadays, the availability of high-precision isotope ratio mass spectrometers combined with sensitive field tracer method (Montoya et al., 1996) makes it feasible to carry out $^{15}N_2$-tracer incubations on unconcentrated natural water samples, with minimal disturbance of the system. But actually, such measurements of N_2-fixation in oceanic waters are rare and data reported here are the first available for the South Pacific. Oceanic waters of south Pacific seem to be a favourable region for diazotrophy, which is observed at significant rates in surface throughout the transect. N_2-fixation appeared the weakest but the most stable biological process along the 8000 km investigated area, in spite of large deviation in nutrients biomass and primary productivity. In the SPG, the N_2-fixation was essentially located in the upper layer (0–50 m), where the irradiance is higher and atmospheric inputs, even very weak in this region are certainly more available. Unfortunately, the organisms responsible of this process remain unidentified in the present study. Regardless the absence of diazotrophic *Trichodesmium* populations during the cruise we can postulate that N_2-fixation was certainly performed by nanoplanktonic organisms, recently revealed by new molecular biological techniques (Zehr et al., 1998, 2000). Zehr et al. 2001) found small (2–3 μm in diameter) unicellular cyanobacteria expressing gene *nifH* in the subtropical North Pacific, associated with significant nitrogen accumulation (0.008–0.016 nmol $L^{-1}h^{-1}$). The discovery of other potentially important marine diazotrophs than *Trichodesmium* is opening a new window on the importance of nitrogen fixation in the ocean. Due to their ability to fix N, these nanoplanktonic cyanobacteria can contribute substantially to the input of new nitrogen in to the nutrient-poor water, even if the rates of fixation measured are typically quite

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low relative to the apparent N demand of the ecosystem. Our integrated values (30–910 μmol $m^{-2}d^{-1}$) are on the same order of magnitude than the very scarce values actually available in the literature concerning dinitrogen fixation by nanoplankton, if we except the high value (3955 μmol $m^{-2}d^{-1}$) found along the Australian a coasts by Montoya et al. (2004). Zehr et al. (2001) give an integrated of 92 μmol m^{-2} 12 h^{-1} for the North Pacific. This value is a little higher than those measured by Montoya et al. (2004) in the same region (24–66 μmol $m^{-2}d^{-1}$). Similar results have been found in the South-west Pacific around the New Caledonia (Garcia et al., 2007), with nitrogen fixation in the <10 μm fraction, e.g. not associated with *Trichodeminum* populations, ranged from 40–300 μmol $m^{-2}d^{-1}$. Falcon et al. (2002), including night fixation found a daily range of 62–167 μmol $m^{-2}d^{-1}$ for the north Atlantic. And recent equivalent rates ($\approx$ 50 μmol $m^{-2}d^{-1}$) were obtained in Mediterranean Sea during the oligotrophic summer period (Garcia et al., 2006), representing up to 40% of new production. N_2-fixation sustained a large fraction of new production (up to 100%) in this oligotrophic environment and this nitrogen pool represents a potentially important nitrogen source for other organisms in the pelagic food web, especially in the oligotrophic waters where any input of other form of new nitrogen is excluded: the vertical flux of nitrate from below the thermocline is extremely low due to the deep of the thermocline; and potential atmospheric deposition of nitrogen and phosphorus is almost absent according to the aerosols measurements performed in this area by Jickells et al. (2005). Then, in agreement with observations made in the North Pacific Gyre where nitrogen fixation is a major source of newly fixed nitrogen to the photic layer (Karl et al., 1997), the N-deficiency SPG would provide an ideal ecological niche for the proliferation of N_2-fixing unicellular cyanobacteria, even if our estimated rates were 6 fold lower than this expected from a biogeochemical model (120 mmoles $m^{-2}.y^{-1}$) by Deutsch et al. (2007).

All along the investigated area, primary production appears quantitatively related to new production (Fig. 9), so that the measurement of total production based on photosynthetic assimilation can be used to provide preliminary estimates of new production, and use for modeling purposes. The model predicts that a threefold increase of total

production in oligotrophic waters would result in a tenfold increase of new production. Such a relationship between primary production and new production agrees well with data from Dugdale et al. (1992) and Raimbault et al. (1999) for the equatorial Pacific (until 16° S), but were much lower (up to 10 fold) than those estimated by model of Eppley and Peterson (1979). More, in this very oligotrophic water and although strong nutrients gradient, we don't find an evident pattern between nitrate concentration and new production as suggested by Platt and Harrison (1985). When mean values of *f* ratio are plotted versus integrated primary productivity rates there is a positive logarithmic relationship (Fig. 10). The initial slope (0.0003) for new production <500 $mg.m^{-2}.d^{-1}$ (≈200 $mg.m^{-2}.y^{-1}$) is close this found by Dugdale et al. (1992) in the equatorial Pacific (0.00063±0.00036), but much lower than 0.0025 proposed by Eppley and Peterson (1979). Then the model proposed by Eppley and Peterson (1979) certainly fails for these oceanic waters, because nitrate uptake in the coastal region is distinct from that on oligotrophic waters.

Only if suitable time scales are considered, the *f* ratio provides an indirect estimation of export rates of particulate organic matter toward the deep ocean. This concept is supported by the assumption that the input by advection of nitrate toward the surface should be balanced by the losses to the deep of particulate and dissolved matter. Sinking fluxes of POC (0.14–1.15 $mgC.m^{-2}.d^{-1}$) and PON (0.04–0.2 $mgN.m^{-2}.d^{-1}$) measuring in the SPG by sediment trap (J. C. Miquel, personal communication) appears much lower that our new production rates obtained with tracer uptake (7–8 mg $C.m^{-2}.d^{-1}$; 1.7 mg $N.m^{-2}.d^{-1}$). Several reasons are often evoked to explain this discrepancy often observed. One of these is the vertical transport of dissolved organic matter (by vertical mixing or horizontal advection) which can exceed fluxes of sinking particles and thus appear as major fate of new production (Copin-Montégut-and Avril, 1993; Peltzer and Hayward, 1996). According to Toggweiler (1989), the most realistic balance is obtained when half of the new production due to upwelled nutrient goes into a pool of dissolved organic compounds. In fact, our data demonstrated that a significant part of the DIN taken up was lost as dissolved organic nitrogen (DON) during the

24 h incubation experiments. It is difficult to ascertain whether the ^{15}N-tracer detected in the DON pool was transferred solely via direct and active release from living phytoplankton cells. The ^{15}N excess enrichment in the DON pool may have also result from cell rupture by sloppy-feeding, and from cells lysis by viral infection (Bronk et al., 1994; Procter and Fuhrman, 1990). Pooling all of available data, DI^{15}N ultimately found in the extracellular DON pool (ρ_{loss}) represented on average 13 to 15% for nitrate and ammonium, respectively. But values were often higher in the SPG, up to 46% in a subsurface layer. It appears that ρ_{net}:ρ_{gross} ratio were in the range of values found in literature, e.g. between the low loss rates (<15%) found in the equatorial Pacific (Raimbault et al., 1999; Raimbault et al., 2000) and the very high ones (74%) found in the Southern California Bight by Bronk and Glibert (1991). They are also in the same order of magnitude than those found in the Mediterranean Sea during spring (Diaz and Raimbault, 2000) and in the Atlantic Ocean (Fernandez and Raimbault, 2007).

But, one should keep in mind that ρ_{loss} does not represent the total flux of nitrogen from the particulate organic matter (PON) to the DON pool. The true DON release (ρ_{DON}) is greater than our measured loss of DIN (ρ_{loss}). Quantification of ρ_{DON} depends on the ^{15}N enrichment in the intracellular DON (R_{DONi}). R_{DONi} is not experimentally accessible, but it is related to the initial ^{15}N enrichment DIN pool (R_{DIN}) according the relation defined by Raimbault et al. (2000),

$$\rho_{DON} = \rho_{loss} \times R_{DIN}/R_{DONi} \quad (9)$$

Because of the dilution of the ^{15}N tracer by intracellular nitrogen during uptake R_{DIN}/R_{DONi} is higher than 1. Then, this relationship indicates that 1) the total fluxes of organic nitrogen from particulate matter to extracellular DON would be higher than the loss of tracer in the form of DON as measured here and 2) lower is the final enrichment of intracellular DON pool greater in the difference between DIN loss and DON release. Assuming phytoplanktonic growth rates calculating from the residence time of chlorophyll-containing particles (Raimbault et al., 2007), R_{DIN}/R_{DONi} ratio would be 3 to 6 fold higher in the SPG than in the productive regions (Marquesas Islands and

Chilean upwelling). Consequently, we can hypothesize that the production of DON was proportionally much higher in the oligotrophic waters than in productive system.

Similar data on dissolved organic carbon (DOC) release are not yet available for this region. However, DOC loss has been observed during field experiments with ^{14}C (Karl et al., 1998) and it is worthwhile to note that nitrogen loss rates obtained here were comparable to release rates found for recently fixed photosynthetic products during photosynthesis (Mague et al., 1980), e.g. for dissolved organic carbon (DOC). It is now well–known that under nutrient limitation, as during summer stratification, large amounts of dissolved organic matter can be produced and accumulated in the upper layer of temperate waters (Buttler et al., 1979; Maita and Yanada; 1990; Libby and Wheeler, 1997), until they disappeared from the surface layer during destratification and winter mixing (Copin-Montegut and Avril, 1993; Carlson et al., 1994). This assumption is strengthened by the fact that a large concentration of carbon-rich dissolved organic matter (C/N=16–23) occurred between 125° W and 95° W (Raimbault et al., 2007), which appears inversely and exponentially related to the primary production (Fig. 11). Annual convection mixing is excluded in the SPG, and due to low horizontal advection, the dissolved organic matter released by primary producers can be accumulated for a long time, reaching levels never yet measured in oceanic waters. Only a small fraction of the primary production (4%) can be exported in term of DOC by turbulent diffusion (Raimbault et al., 2007). Therefore, in spite of low primary production and very low new production, the net biological effect of the SPG in the CO_2 trapping should be not as weak as expected. These results support the conclusion that the SPG system is locked into a strong grazing loop where primary producers are trapped into small-sized, low sinking rate-group of species acting in a very efficient regeneration loop. It is well known that small particles are more strongly retained in the euphotic layer of unproductive oligotrophic areas than in the euphotic layer of productive areas (Lohenz et al., 1992). Small phytoplankton cells are consistent with high grazing rate, e.g. favouring DOM release, since small cells sink slowly and are more likely to be grazed within the euphotic zone. The exceptional huge size of the South

Pacific Gyre, the distance from terrestrial sources of volatile compounds, the long residence time of the quiescent waters accumulated inside the anticyclonic circulation, and the depth of the nitracline are probably favorable to maintain an active microbial loop with a long residence time of organic matter, where new nitrogen is essentially brought by dinitrogen-fixation. As suggested by Thingstad et al. (1997), such microbial loop acting under some nutrient limitation can drive of large accumulation of carbon-rich dissolved organic matter due to over consumption of carbon (Kähler and Koeve, 2001), which is likely to the origin of this paradoxical property of the South Pacific gyre.

5 Conclusions

These results thus demonstrate the very unique character of the ultraoligotrophic South Pacific Gyre (SPG) and its borders, and lead to a number of questions. Primary productivity as well as new production was the lowest ever measured in the ocean, and can be considered as an end point for trophic level. A large part of new primary production was fuelled by N_2-fixation, rather than deep nitrate diffusing from deeper layer into the photic zone. As a consequence *f* ratio appeared often close to zero, essentially sustained by nitrogen fixation acting at very low rate and leading to very weak particulate export. The productive system seemed to be maintained by an efficient loop of regeneration, active over the whole photic layer and leading to overconsumption of carbon. Then, in spite of very low primary productivity, the SPG could accumulate new carbon from the atmosphere in terms of dissolved organic carbon (DOC). According to the long-term fate of this accumulated of DOC, SPG could be a sink for atmospheric CO_2.

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References

Allen, A. E., Howard-Jones, M. H., Booth, M. G., Frischer, M. E., Verity, P. G., Bronk, D. A., and Sanderson, M. P.: Importance of heterotrophic bacterial assimilation of ammonium and nitrate in the Barents Sea during summer, J. Marine. Syst. 38, 93–108, 2002.

Altabet, M.: Organic C, N and stable isotopic composition of particulate matter collected on glass-fibber and aluminum oxide filters, Limnol. Oceanogr., 35, 902–909, 1990.

Aufdenkampe, A. K., McCarthy, J. J., Rodier, M., Navarrette, C., Dunne, J., and Murray, J. W.: Estimation of new production in the Tropical Pacific, Global. Biogeochem. Cycles., 15, 101–113, 2001.

Aufdenkampe, A. K., McCarthy, J. J., Navarrette, C., Rodier, M., Dunne, J., and Murray, J. W.: Biogeochemical controls on new production in the tropical pacific, Deep. Sea. Res.II., 49, 2619–2648, 2002.

Bianchi, M., Feliatra, F., Tréguer, P., Vincendeau, M., Morvan, J.: Nitrification rates, ammonium and nitrate distribution in upper layers of the water column and in sediments of the Indian sector of the Southern Ocean, Deep Sea Res. II., 44, 1017–1032, 1997.

Bode, A., Castro, C., Doval, M. D., and Varela, M.: New and regenerated production and ammonium regeneration in the western Bransfield region (Antarctica) during phytoplankton bloom conditions in summer, Deep sea Res. II, 49, 787–804, 2002.

Bronk, D. A. and Glibert, P. A: ^{15}N tracer method for the measurement of dissolved organic nitrogen release by phytoplankton, Mar. Ecol. Prog. Ser. 77, 171–182, 1991.

Bronk, D. A., Glibert, P., and Ward, B. B.: Nitrogen uptake, dissolved organic nitrogen release and new production, Science, 256, 1843–1846, 1994.

Buttler, E. I., Knos, S., and Liddicoat, M. I.: The relationship between inorganic and organic nutrients in seawater, J. Mar. Environm. Ass. U.K., 59, 239–250, 1979.

Capone, D. G. and Carpenter, E. J.: Nitrogen fixation in the marine environment, Science, 217, 1140–114, 1982.
Capone D. G., Burns J.A, Montoya, J. P., Subramaniam, A., Mahaffey, C., Gunderson, T., Michaels, A. F., and Carpenter, E. J.: Nitrogen fixation by Trichodesmium spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean, Global Biogeochem. Cy., 19, GB2024, 2005.
Carlson C. A., Ducklow H. W., and Michaels, A. F.: Annual flux of dissolved organic carbon from theeuphotic zone in thenorthwestern Sargasso Sea. Nature, 371, 405–408, 1994.
Chavez, F. P., Buck, K. R., Bidigare, R. R., Karl, D. M., Hebel, D., Latasa, M., and Campbell, L.: On the chlorophyll a retention properties of glass-fiber GF/F filters, Limnol. Oceanogr., 40, 428–433, 1995.
Chavez, F. and Barber, R.: An estimate of new production in the equatorial Pacific, Deep Sea Res., 34, 7, 1229–1243, 1987.
Charpentier, J., Farias, L., Yoshida, N., Boontanon, N., and Raimbault, P.: Nitrous oxide distribution and its origin in the central and eastern South Pacific subtropical, Gyre, Biogesciences Discuss., 4, 1673–1702, 2007.
Clark, L., Ingall, E. D., and Bener, R.: Marine organic phosphorus cycling: Novel insights from nuclear magneticresonance, Amer. J. Sci., 2999, 724–737, 1999.
Claustre, H. and Maritorena, S.: Ocean Science: The many shades of ocean blue, Science, 302, 1514–1515, 2003.
Codispoti, L. A. and Christensen, J. P.: Nitrification, denitrification and nitrous oxide cycling in the eastern tropical, South Pacific Ocean. Mar. Chem., 16, 4, 277–300, 1985.
Copin-Montégut, G. and Avril, B.: Vertical distribution and temporal varaition of dissolved organic carbon in the North-Western Mediterranean Sea, Deep-Sea Res., 40, 1963–1972, 1993.
Dandonneau, Y., Montel, Y., Blanchot, J., Giraudeau, J., and Neveux, J.: Temporal variability in phytoplankton pigments, picoplankton and coccolithophores along a transect through the North Atlantic and tropical southwestern pacific, Deep Sea Res. I, 53, 689–712, 2006.
Daneri, G. and Quinones, R. A.: Undersamples ocean systems: appeal for an international study of biogeochemical cycles in the Southern Pacific gyre and its boundaries, U.S. JGOFS Newsletter January 2001, 9, 2001.
Deutsch, C., Sarmiento J. L., Sigman D. M., Gruber N., and Dunne, J. P.: Spatial coupling of nitrogen inputs and losses in the ocean, Nature, 445, 163–167, 2007.

Diaz, F. and Raimbault, P.: Nitrogen regeneration and dissolved organic nitrogen release during spring in a NW Mediterranean coastal zone (Gulf of Lions): implications for the estimations of f ratio and new production, Mar. Ecol. Progr. Ser., 197, 53–66, 2000.
Dugdale, R. C. and Goering, J. J.: Uptake of new and regenerated forms of nitrogen in primary productivity, Limnol. Oceanogr. 12, 196–206, 1967.
Dugdale, R. W. and Wilkerson, F. P.: The use of ^{15}N to measure nitrogen uptake in eutrophic oceans: experimental considerations, Limnol. Oceanogr., 31, 673–689, 1896.
Dugdale, R. W., Wilkerson, F. P., Chavez, F. P., and Barber, R. T.: Estimating new production in the equatorial Pacific at 150° W., J. Gephys. Res., 97, 681–686, 1992.
Donald, K. M., Joint, I., Rees, A. P., Malcom, E., Woodward, S., and Savidge, G.: Uptake of carbon, nitrogen and phosphorus by phytoplankton along the 20° W meridian in the NE Atlantic between 57.5° N and 37° N, Deep Sea Res., 48, 873–897, 2001.
Dore, J. E. and Karl, D. M.: Nitrification in the euphotic zone as a source of nitrite, nitrate, and nitrous oxide at Station ALOHA, Limnol. Oceanogr., 41, 1619–1628, 1996.
Dore, J. E., Brum, J. R., Tupas, L. M., Karl, D. M.: Seasonal and interannual variability in sources of nitrogen supporting export in the oligotrophic subtropical, North Pacific Ocean. Limnol. Oceanogr., 47, 6, 1595–1607, 2002.
Dugdale, R. C. and Goering J. J.: Uptake of new and regenerated forms of nitrogen in primary productivity, Limnol. Oceanogr., 12, 196–206, 1967.
Dugdale, R. C. and Wilkerson, F. P.: The use of ^{15}N to measure nitrogen uptake in eutrophic oceans, experimental considerations, Limnol. Oceanogr., 31, 4, 673–689, 1986.
Dugdale, R. C., Wilkerson, F. P., Barber, R., and Chavez, F.: Estimating new production in the equatorial Pacific Ocean at 150° W, J. Geophys. Res., 97, (C1), 681–686, 1992.
Eppley, R. W. and Peterson B. J.: Particulate organic matter flux and planktonic new production in the deep ocean, Nature, 282, 677–680, 1979.
Eppley, R. W. and Renger, E. H.: Nitrate utilization by plankton in the equatorial pacific march 1988 along 150° W., J. Geophys. Res., 97, 663–668, 1992.
Falcon, L. I., Carpenter, E. J., Cipriano, F., Bergman, B., Capone, D. G.: N_2fixation by unicellular bacterioplankton from the Atlantic and pacific oceans: phylogeny and in situ rates, Appl. Environ. Microbiol., 765–770, 2004.
Falkowski, P. G., Barber, R. T., Smetacek V., et al.: Biogeochemical controls and feedbacks onprimary production, Science, 281, 20–206, 1998.
Faul, K. L., Paytan, A., and Delaney, M. L.: Phosphorus distribution in sinking oceanic particu-

late matter, Mar. Chem., 97, 307–333, 2005.
Fernandez, C. and Raimbault, P.: Nitrogen regeneration in the NE Atlantic Ocean and its impact on seasonal new, regenerated and export production, Mar. Ecol., Progr. Ser., 337, 79–92, 2007.
Frazel, D. W. and Berberian, G.: Distribution of chlorophyll and primary productivity in relation to water column structure in the North Atlantic Ocean, Global Biogeochem. Cycles, 4, 241–251, 1990.
Fuhrman, J. A., Sleeter, T., and Carlson, C.: Oligotrophic ocean biomass is dominated by non –photosynthetic bacteria, even in euphotic zone, EOS, 68, 1729, 1987.
Galloway, J. N., Schlesinger, W. H., Levy, H., Michaels, A., and Schnoor, J. L.: Nitrogen fixation: Anthropogenic enhancement-environmental response, Glob. Biogeochem. Cycles, 9, 235–252, 1995.
Garcia, N., Raimbault, P., and Sandroni, V.: Seasonal nitrogen fixation and primary production in Southwest Pacific (New Caledonia): Some evidence for nanoplanktonic diazotrophy and rapid transfer of newly fixed nitrogen to picoplankton organisms, Mar. Ecol. Progr. Ser., 343, 25–33, 2007.
Gentilhomme, V. and Raimbault, P.: Absorption et régénération de l'azote dans a zone frontale du courant algérien (Méditerranée Occidentale): Réévaluation de la production nouvelle, Oceanol. Acta. 17, 555–562, 1994.
Glibert, P. M., Lipschultz, F., McCarthy, J. J., and Altabet, M. A.: Isotope dilution models of uptake and remineralization of ammonium by marine plankton, Limnol. Oceanogr. 27, 639–650, 1982.
Grob, C., Ulloa, O., Claustre, H., Alarcon, G., Huot, Y., and Marie, D.: Contribution of picoplankton to the particulate attenuation coefficient (cp) and organic carbon concentration (POC) in the eastern South pacific, Biogeosciences Discuss., 4, 1461–1497, 2007, http://www.biogeosciences-discuss.net/4/1461/2007/.
Harrison, W. G., Platt, T., and Lewis, M. R.: *f*-ratio and its relationship to ambient nitrate concentration in coastal waters, J. Plankton Res., 9,(1), 235–248, 1987.
Harrison, W. G., Harris, L. R., and Irwin, B. D.: The kinetic of nitrogen utilization in the oceanic mixed layer: nitrate and ammonium interactions at nanomolar concentrations, Limnol. Oceanogr., 41, 16–32, 1996.
Holmes, M. R., Aminot, A., Kerouel, R., Hooker, B. A., and Peterson, J. B.: A simple and precise method for measuring ammonium in marine and freshwater ecosystems, Can. J. Fish Aquat.

Sci., 56, 1801–1808, 1999.
Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P. W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P. S., Mahowald, N., Prospero, J. M., Ridgwel, A. J., Tegen, I., and Torres, R.: Global iron connections between desert dust, ocean biogeochemistry and climate, Science, 308, 67–71, 2005.
Karl, D. M.: Nutrients dynamics in the deep blue sea, Trends in microbiology, 10, 410–418, 2002.
Karl, D. M., Letelier, R., Tupas, L., Dore, J., and Christian, J. D. H.: The role of nitrogen fixation in biochemical cycling in the subtropical North Pacific Ocean, Nature, 386, 533–538, 1997.
Kähler, P. and Koeve, W.: Marine dissolved organic matter: can its C:N ratio explain carbon over consumption?, Deep-sea Res. I, 48, 49–62, 2001.
Kustka, A. B., Carpenter, E. J., Sanudo-Wilhelmy, S., Burns, J., Capone, D., and Sunda, W. G.: Iron requirements for N_2 and NH_4 supported growth in cultures of Trichodesmium (IMS 101): Comparison with nitrogen fixation rates and Fe:C ratios of field populations, Limnol. Oceanogr., 48, 1869–1884, 2003.
Laws, E.: Isotope dilution models and themistery of the vanishing 15N., Limnol. Oceanogr., 29, 379–386, 1984.
Libby, P. S. and Wheeler, P. A.: Particulate and dissolved organic nitrogen in the central and eastern Equatorial Pacific, Deep-Sea Res., 44, 345–361, 1996.
Lipschultz, F., Bates, N. R., Carlson, C., and Hansell, D. A.: New production in the Sargasso Sea: History and current status, Global Biogeochem. Cycles., 16, (1), doi:10.1029/2000GB001319, 2002.
Lohrenz, S. E., Knauer S. A., Asper, V. L., Tuel, M., Michaels, A. F., and Knap, A. H.: Seasonal variability in primary production and particle flux in the northwestern Sargasso sea: US JGOFS Bermuda Atlantic Time-Series Study, Deep-Sea Res., 39, 1373–1391, 1992.
Longhurst, A. R.: Ecological geography of the Sea, Academic press, London, 398 pp, 1998.
Mague, T. H., Friberg, E., Hugues, D. J., and Morris, I.: Extracellular release of carbon by marine phytoplankton; a physiological approach, Limnol. Oceanogr., 25, 262–279, 1980.
Maita, Y. and Yanada, M.: Vertical distribution of total dissolved nitrogen and dissolved organic nitrogen in seawater, Geochemical J., 24, 245–254, 1990.
Menzel, D. W. and Ryther, J. H.: The annual cycle of primary production in the Sargasso Sea off Bermuda, Deep Sea Res., 6, 351–367, 1960.

Menzel, D. W. and Ryther, J. H.: The composition of particulate organic matter in the western north Atlantic, Limnol. Oceanogr., 9, 179–186, 1964.
Montoya, J. P., Voss, M., Kähler, P., and Capone, D. G.: A simple, high precision, high sensitivity tracer assay for N_2 fixation, Appl. Environ. Microb., 62, 986–993, 1996.
Montoya, J. P., Holl, C. M., Zehr, J. P., Hansen, A., Villareal, T. A., and Capone, D. G.: High rates of N_2 fixation by unicellular diazotrophs in the oligotroph Pacific, Nature, 430, 1027–1031, 2004.
Moore, J. K., Doney, S. C., Glover, D. M., and Fung, I. Y.: Iron cycling and nutrient limitation patterns in surface waters of the world ocean. Deep-sea res., part II, 49, 463–507, 2002.
Morel, A. and Maritorena, S.:Bio-optical properties of oceanic waters: a reappraisal, J. Geophys. Res., 106(C4), 7163–7180, 2001.
Morel, A., Gentili, B., Clauster, H., Babin, M., Bricuad, A., Ras, J., and Tieche, F.: Optical properties of the clearest natural waters, Limonl. Oceanogr. 52, 217–229, 2007.
Nixon, S. W.: Coastal eutrophication: a definition, social causes and future concerns, Ophelia, 41, 199–220, 1995.
Peltzer, E. T. and Hayward, N. A.: Spatial and temporal variability of total organic carbon along the 140° W in the equatorial Pacific ocean in 1992, Global Biogeochem. Cycles, 6, 45–76, 1996.
Priscu, J. C. and Downes, M. T.: Nitrogen uptake, ammonium oxidation and nitrous oxide (N_2O) levels in the coastal waters of western Cook Strait, New Zealand, Estuary, Coast Shel Sci., 20, 529–542, 1985.
Procter, L. M. and Fuhrman, J. A.: Viral mortality of marine bacteria and cyanobateria, Nature, 343, 1327–1332, 1990.
Raimbault P., Slawyk, G., Coste, B., and Fry, J.: Feasibility of using an automated colorimetric procedure for the determination of seawater nitrate in the 0 to 100 nM range: Examples from field and culture, Mar. Biol., 104, 347–351, 1990.
Raimbault, P., Garcia, N., and Cerrutti, F: Distribution of inorganic and organic nutrients in the South Pacific Ocean – evidence for long-term accumulation of organic matter in nitrogen-depleted waters, Biogeosciences Discuss., 4, 3041–3087, 2007, http://www.biogeosciences-discuss.net/4/3041/2007/.
Raimbault, P., Slawyk, G., Boudjellal, B., Coatanoan, C., Conan, P., Coste, B., Garcia, N., Moutin, T., and Pujo-Pay, M.: Carbon and nitrogen uptake and export in the equatorial pacific at 150° W: Evidence of an efficient regenerated production cycle, J. Geophys. Res., 104, C2,

3341–3356, 1999.
Raimbault, P., Slawyk, G., and Garcia, N.: Comparison between chemical and isotopic measurements of biological nitrate utilization: further evidence of low new production levels in the equatorial Pacific, Mar. Biol., 136, 1147–115, 2000.
Ras, J., Claustre, H., and Uitz, J.: Spatial variability of phytoplankton pigment distributions in the subtropical South pacific Ocean: a comparison between in situ and modelled data, Biogesciences Discuss., 4, 3409–3451, 2007.
Raven, J. A.: The iron and molybdum use efficiencies of plant growth with different energy, carbon and nitrogen source, New Phytol., 109, 279–287, 1988.
Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of seawater, p. 26–77, in: The Sea Wiley, edited by: M. N. Hill, 1963.
Rees, A. P., Joint I., and Donald, D. M.: Early spring bloom phytoplankton-nutrient dynamics at the celtic Sea Shelf edge, Deep Sea Res., 46, 483–510, 1999.
Ryther, J. H. and Menzel, D. W.: The seasonal and geographical range of primary production in the Western Sargasso sea, Deep Sea Res., 6, 235–238, 1960.
Sahlsten, E.: Nitrogenous nutrition in the euphotic zone of the central North pacific, Gyre. Mar. Biol., 96, 433–439, 1987.
Shaffer, G., Salinas, S., Pizarro, O., Vega, A., and Hormazabal, S.: Currents in the deep ocean off Chile (30° S), Deep-Sea Res., 42, 66–69, 1995.
Slawyk, G. and Collos, Y.: ^{13}C and ^{15}N uptake by marine phytoplankton III. Interactions in euphotic zone profiles of stratified oceanic areas, Mar. Ecol. Prog. Series., 19, 223–231, 1984.
Slawyk, G. and P. Raimbault: Simple procedure for the simultaneous recovery of dissolved inorganic and organic nitrogen in ^{15}N-tracer experiments and improving the isotopic mass balance, Mar. Ecol. Prog. Ser., 124, 289–299, 1995.
Slawyk, G., Raimbault, P., and Garcia, N.: Measuring gross uptake of 15N Labelles nitrogen by marine phytoplankton without particulate matter collaction: Evidence of low 15N losses to the dissolved organic nitrogen pool, Limnol. Oceanogr., 43, 7, 1734–1739, 1998.
Slawyk, G., Raimbault, P., and Garcia, N.: Use of ^{15}N to measure dissolved organic nitrogen release by marine phytoplankton (reply to comment by Bronk and Ward), Limnol. Oceanogr., 45, 8, 1884–1886, 2000.
Smith, S. V.: Phosphorus versus nitrogen limitation in the marine environment, Limnol. Oceanogr., 29, 1149–1160, 1983.

Sokal, R. R. and Rohlf, F. J.: Biometry, The principles and practice of statistics in biological research, WH Freeman and Company, New-York, 1995.
Thingstad, T. F., Hagstrom A., and Rassoulzadegan, F.: Accumulation of degradable DOC in surface waters: is it cause by malfunctionning microbial loop?, Limnol. Oceanogr., 42, 398–404, 1997.
Tréguer, P. and LeCorre, P.: Manuel d'analyses des sels nutritifs dans l'eau de mer: Utilisation de l'Autoanalyser II Technicon. Univ. of Bretagne Occidentale, Lab. de Chim. Mar., Brest, France, 1975.
Ward, B. B.: Light and substrate concentrations relationships with marine ammonium assimilation and oxidation rates, Mar. Chem. 16, 4, 301–316, 1985.
Ward, B. B.: Nitrogen transformations in the Southern California Bight, Deep Sea Res., 34, 785–805, 1987.
Ward, B. B.: Nitrification and the marine nitrogen cycle, in: Microbial ecology of the oceans, edited by: D. Kirchman , Wiley-Liss Inc., pp. 427–454, 2000.
Ward, B. B., Talbot, M. C., and Perry, M. J.: Contributions of phytoplankton and nitrifying bacteria to ammonium and nitrite dynamics in coastal waters, Cont. Shelf. Res, 3, 383–398, 1984.
Ward, B. B., Kilpatrick, K. A., Renger, E. H., and Eppley, R. W.: Biological nitrogen cycling in the nitracline, Limnol. Oceanogr., 34, 3, 493–513, 1989.
Ward, B. B. and Zafiriou, O. C.: Nitrification and nitric oxide in the oxygen minimum of the eastern tropical North Pacific, Deep Sea Res., 35, 7, 1127–1442, 1988.
Weiss, R. F.: The solubility of nitrogen, oxygen and argon in water and seawater, Deep Sea-Res., 17, 721–735, 1970.
Woodward, E. M. S. and Rees, A. P.: Nutrient distributions in an anticyclonic eddy in the northeast Atlantic Ocean, with reference to nanomolar ammonium concentrations, Deep Sea Res., 48(4–5), 775–794, 2001.
Zafiriou, O. C., Ball, L. A. , and Hanley, Q.: Trace nitrite in oxic waters, Deep Sea Res, 39(7/8A), 1329–1348, 1992.
Zehr, J. P., Mellon, M. T., and Zani, S.: New nitrogen fixing microorganisms detected in oligotrophic oceans by the amplification of nitrogenase (nifH) genes, Appl. Environ. Microbiol., 64, 3444–3450, 1998.
Zehr, J. P., Carpenter, E. J., and Villareal, T. A.: New perspectives on nitrogen-fixing microorganisms in tropical and subtropical oceans, Trends Microbiol., 8, 68–73, 2000.

Zehr, J. P. and Ward, B. B.: Nitrogen cycling in the Ocean: New perspectives on processes and paradigms, Appl. Environ. Microbiol., 68, 3, 1015–1024, 2002.
Zehr, J. P. and Ward, B. B.: Nitrogen cycling in the ocean: new Nitrogen cycling in the ocean: new perspectives on processes and paradigms, Appl. Environm. Microbial., 68, 1015–1024, 2002.
Zehr, J. P., Waterbury, J. B., Turner, P. J., Montoya, J. P., Omoregie, E., Steward, G. F., Hansen, A., and Karl, D. M.: Unicellular cyanobacteria fix N_2 in the subtropical North Pacific Ocean., Nature, 412, 635–638, 2001.

Table 1. Percentages (mean values integrated over the photic layer) of ammonium uptake in the <GF/F fraction ($\rho_{<GF/F}$) and loss in term of DON ($\rho_{DON<0.2\,\mu m}$) from ammonium and nitrate relative to gross uptake rates ($\rho_{gross}=\rho net + \rho_{DON<0.2\,\mu m}$) for the five investigated oceanic regions. Values from nitrate values are available from only in situ profiles performed on the 5 experimental sites.

	Ammonium % ρ_{gross}			Ammonium % ρ_{gross}		Nitrate %ρ_{gross}
Area	$\rho_{<GF/F}$	$\rho_{DON<0.2\,\mu m}$	Experimental site	$\rho_{<GF/F}$	$\rho_{DON<0.2\,\mu m}$	$\rho_{DON<0.2\,\mu m}$
MAR (141°–134° W)	7±4	4±2	12° S–138° W	6±3	4±2	11±4
HNL (133°–123° W)	17±14	10±9	9° S–136° W	7±4	1±1	10±7
SPG (123°–101° W)	41±19	28±13	26° S–114° W	26±14	20±7	19±12
EGY (100°–81° W)	25±15	15±13	32° S–91° W	16±14	12±7	11±9
UPW (80°–72° W)	26±36	12±9	34° S–73° W	55±61	16±14	12±8

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Table 2. Mean and standard deviation of integrated rates over the photic layer of nitrate (ΣNO_3), primary production (ΣPP), nitrate uptake ($\Sigma\rho_{NO_3}$), ammonium uptake ($\Sigma\rho_{NH_4}$), nitrogen fixation ($\Sigma\rho_{N_2}$), carbon/nitrogen ratio during uptake (C/N), heterotrophic ammonium uptake ($\Sigma H\rho_{NH_4}$), ammonium regeneration (r_{NH_4}) and nitrification (ρ_{NIT}) pooled for each studied oceanic area.

Area	ΣNO_3 mmoles.m^{-2}.d^{-1}	ΣPP g.m^{-2}.d^{-1}	$\Sigma\rho_{NO_3}$	$\Sigma\rho_{NH_4}$ mmoles.m^{-2}.d^{-1}	$\Sigma\rho_{N_2}$	C/N	$\Sigma H\rho_{NH_4}$	Σr_{NH_4} mmoles.m^{-2}.d^{-1}	$\Sigma\rho_{NIT}$
MAR(141°–134° W)	128±24	0.74±0.1	2.2±1.1	8.7±3.6	0.11±0.03	6.3±2.6	6.3±1.6	5.8±1.9	0.82±0.69
HNL(133°–123° W)	49±73	0.25±0.12	0.5±0.7	4.6±4.3	0.07±0.07	5.2±2.2	2.6±0.8	4.8±3.1	0.61±0.7
SPG(123°–101° W)	0.92±1.3	0.10±0.07	0.06±0.06	2.1±1.0	0.06±0.03	6.1±2.3	1.2±0.6	3.5±1.9	0.76±0.4
EGY(100°–81° W)	158±170	0.36±0.6	0.82±0.4	6.0±2.3	0.03±0.005	4.4±1.4	2.9±0.4	6.3±2.0	0.81±0.57
UPW(80°–72° W)	285±310	1.8±1.3	8.6±7	20±10	0.91±0.06	4.9±0.9	6.2±2.0	19±11	1.31±06

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Table 3. Mean and standard deviation of integrated rates over the photic layer of chlorophyll *a*(ΣTchlo), *f* ratio calculated with net uptake rates of dissolved inorganic nitrogen (f_{net}), new production calculated by multiplied rates of dissolved inorganic nitrogen rates by the Redfield ratio 6.6 (New PP) or by multiplying the primary production by the *f* ratio (PP x f) for the five investigated oceanic regions. Mean "net *f* ratio" (f_{net}) and "gross *f* ratio" (f_{gross}) are compared with data obtained during in situ experiments performed at 5 experimental sites.

Area	ΣTchlo $mg.m^{-2}.d^{-1}$	f_{net} mean	New PP $gC.m^{-2}.d^{-1}$	PP x f $gC.m^{-2}.d^{-1}$	experimental sites	f_{net}	f_{gross}
MAR(141°–134° W)	27±5	0.18±0.04	0.18± 0.10	0.13±0.02	2° S–138° W	0.18	0.19
HNL(133°–123° W)	18±4	0.08±0.04	0.04±0.06	0.02±0.02	9° S–136° W	0.09	0.10
SPG(123°–101° W)	11±2	0.05±0.03	0.008±0.007	0.007±0.007	26° S–114° W	0.05	0.06
EGY(100°–81° W)	16±4	0.12±0.07	0.07±0.03	0.04±0.03	32° S–91° W	0.11	0.11
UPW(80°–72° W)	44±28	0.27±0.08	0.69±0.49	0.53±0.47	34° S–73° W	0.27	0.28

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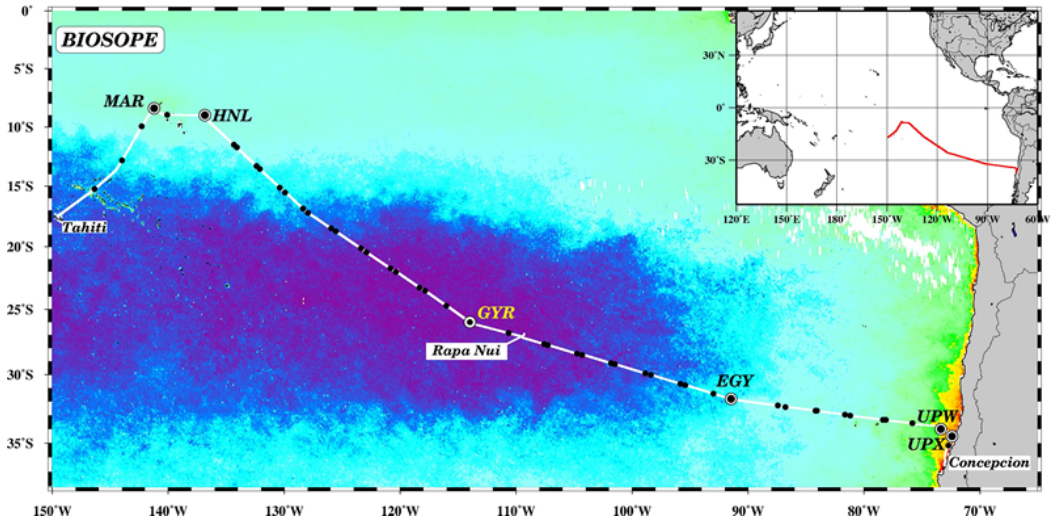

Fig. 1. Map showing the location of the BIOSOPE cruise from Marquises Island to Chile superimposed on a SeaWiFS surface Chl *a* composite (November–December 2004). Locations of CTD casts are indicated by dark points and long time experimental stations by large circles. (MAR = 141,3° W; 8.4° S; HLN = 136.8° W; 9° S; GYR = 114° W, 26° S); EGYR = eastern border of the gyre (91.4° W, 31.8° S; UPW = 73° W–34° S and UPX = 72.4° W–34.5° S).

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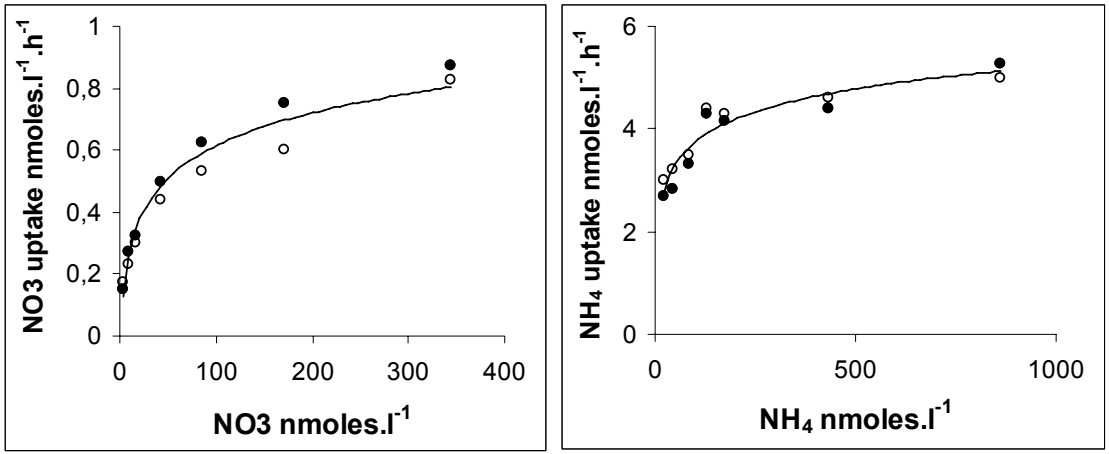

Fig. 2. Rates of nitrate and ammonium uptake (nmoles.l^{-1}.h^{-1}) as function of nitrate and ammonium additions in nutrient depleted waters. Experiments were performed during two successive days with surface waters of the South pacific Gyre (114° W–26° S).

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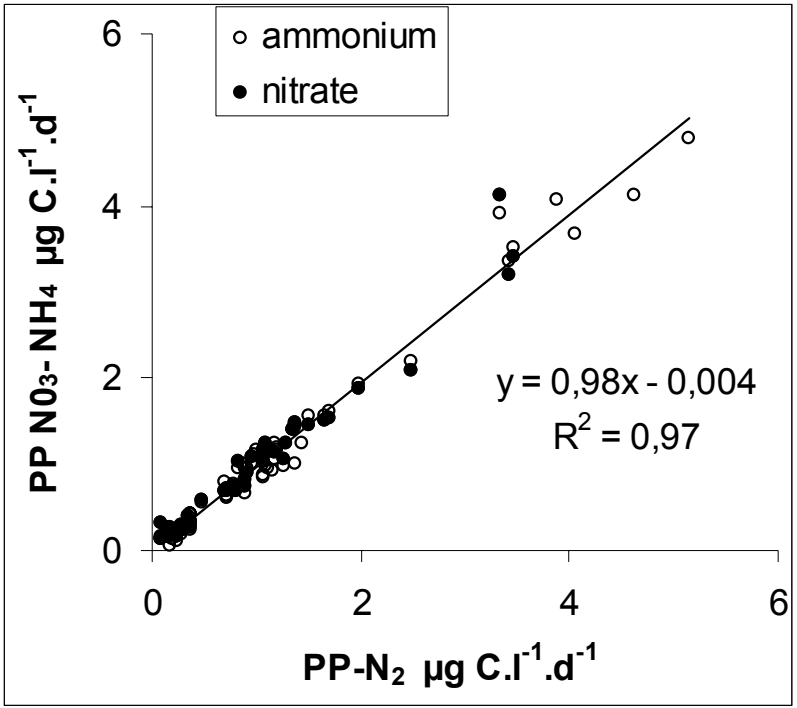

Fig. 3. Comparison between primary production (mgC.m^{-3}.d^{-1}) measured in nutrient-depleted samples, e.g. without nutrients addition (PPN_2), and those (PP NO_3-NH_4) spiked with nitrate (17 nmoles.l^{-1}) or ammonium (43 nmoles.l^{-1}). The solid is line is the model II linear regression.

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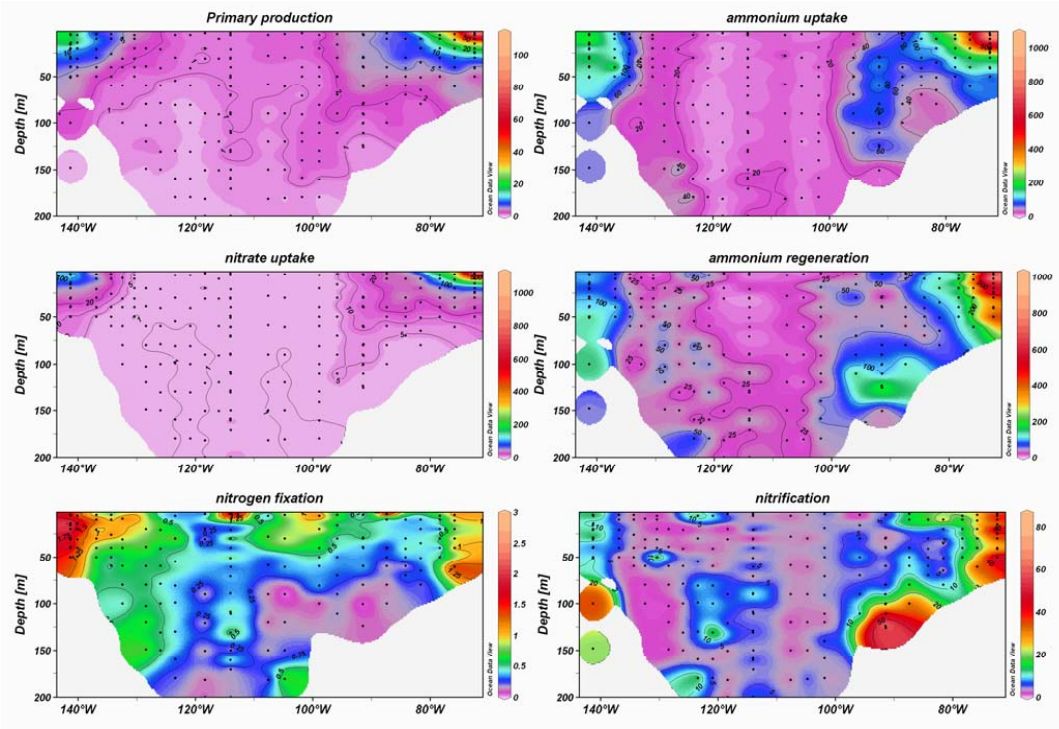

Fig. 4. Longitudinal sections of primary production (μgC.l^{-1}.d^{-1}), nitrate uptake (nmoles.l^{-1}.d^{-1}), ammonium uptake (nmolesN.l^{-1}.d^{-1}), nitrogen fixation (nmolesN.l^{-1}.d^{-1}), ammonium regeneration (nmolesN.l^{-1}.d^{-1}) and nitrification (nmolesN.l^{-1}.d^{-1}), along the BIOSOPE Transect. (Ocean Data View software (ODV), version 3.1, Reiner Schlitzer; http://odv.awi.de).

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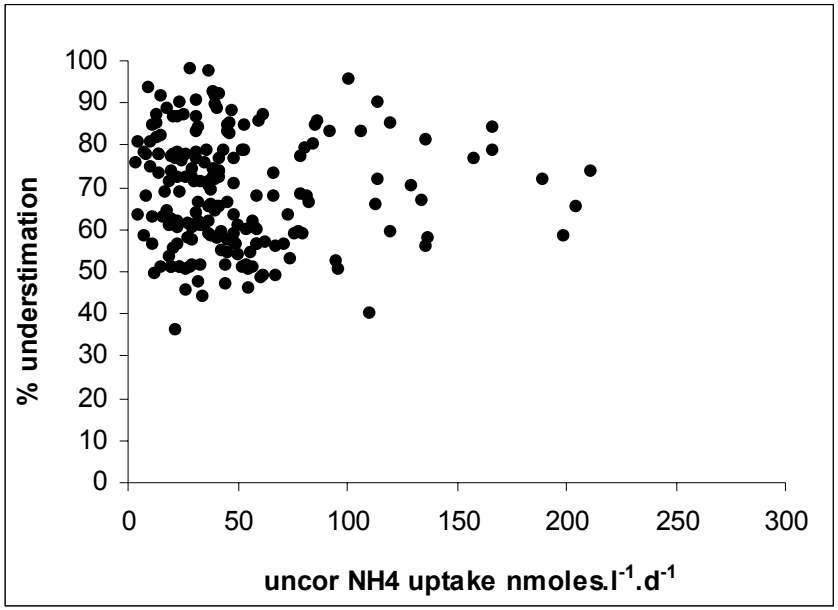

Fig. 5. Percentage of underestimation of ammonium uptake (% underestimation) when isotopic dilution is not included for calculating rates versus ammonium uptake rates no corrected from the isotopic dilution (uncor NH_4 uptake).

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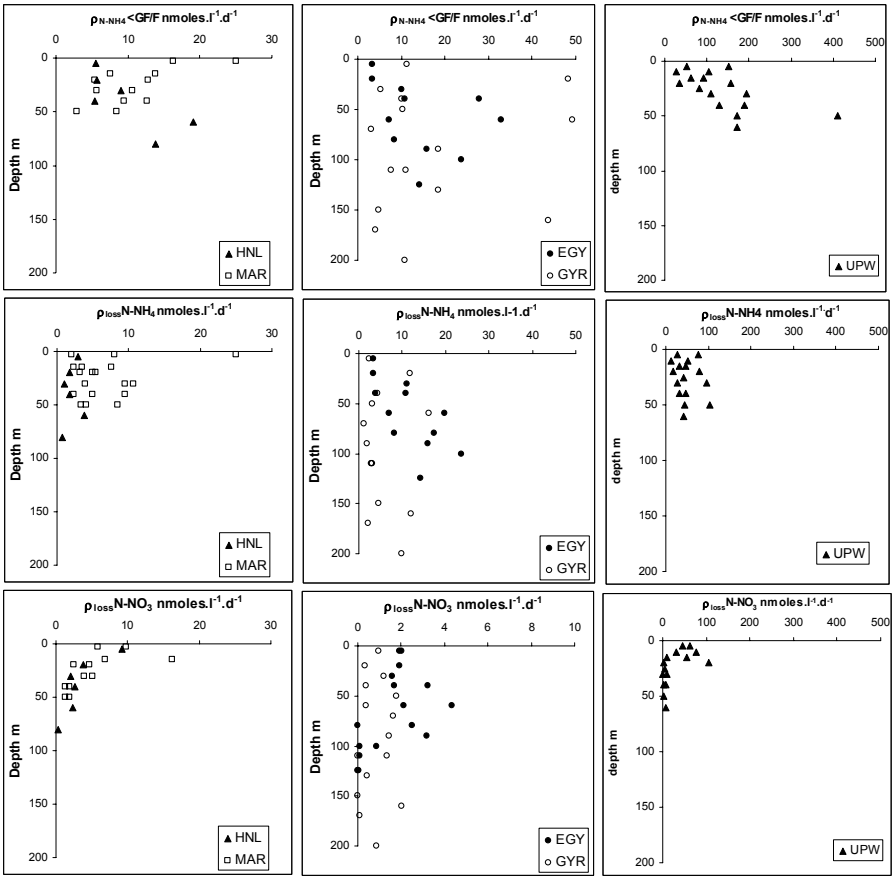

Fig. 6. Vertical profiles of ammonium uptake in the <GF/F fraction (ρ_{NH_4}<GF/F; upper panels), loss of ^{15}N-ammonium in terms of DON in the <0.2 μm fraction (ρ_{loss} NH_4; middle panels) and loss of ^{15}N-nitrate in terms of DON in the <0.2 μm fraction (ρ_{loss} NO_3; lower panels) at the five experimental sites.

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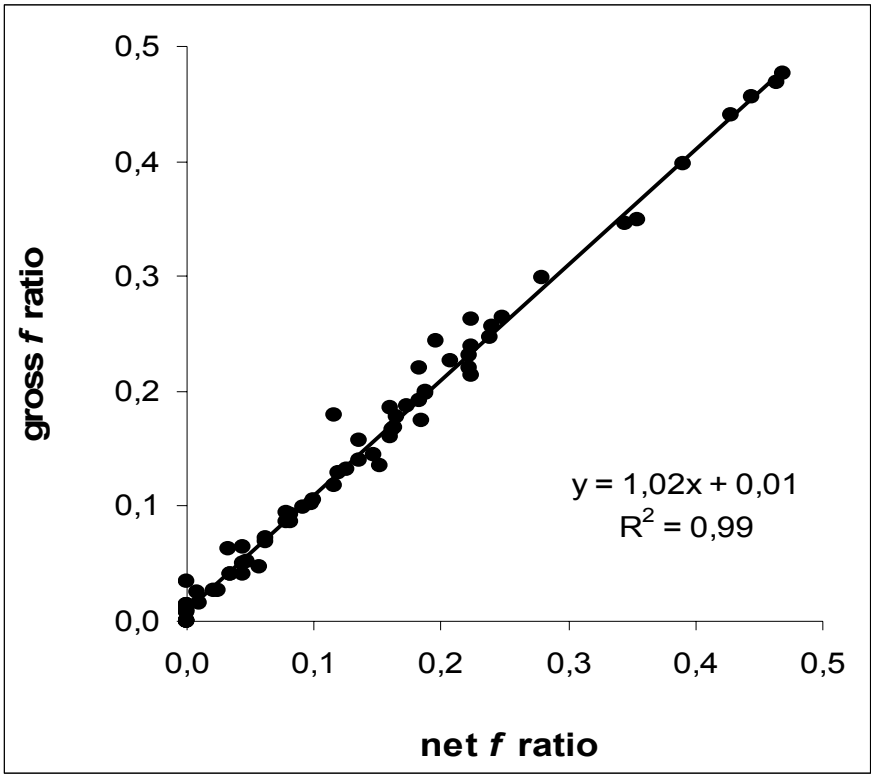

Fig. 7. Comparison of *f* ratio calculating from gross nitrogen uptake (gross *f* ratio) and from net nitrogen uptake rates (net *f* ratio). The linear regression line was obtained from model II regression.

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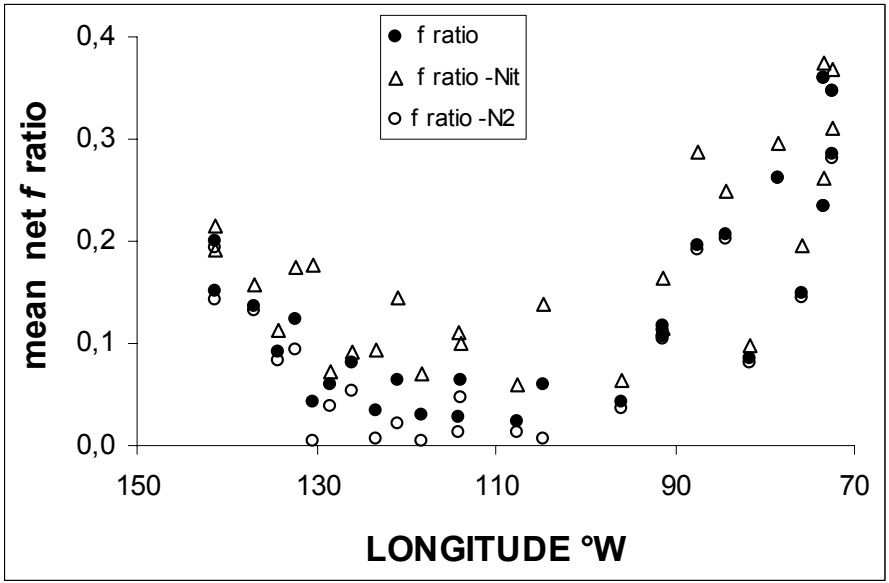

Fig. 8. Longitudinal evolution of net *f* ratio calculating without nitrification (*f* ratio – Nit), without dinitrogen fixation (*f* ratio – N_2), or including the both processes (f ratio).

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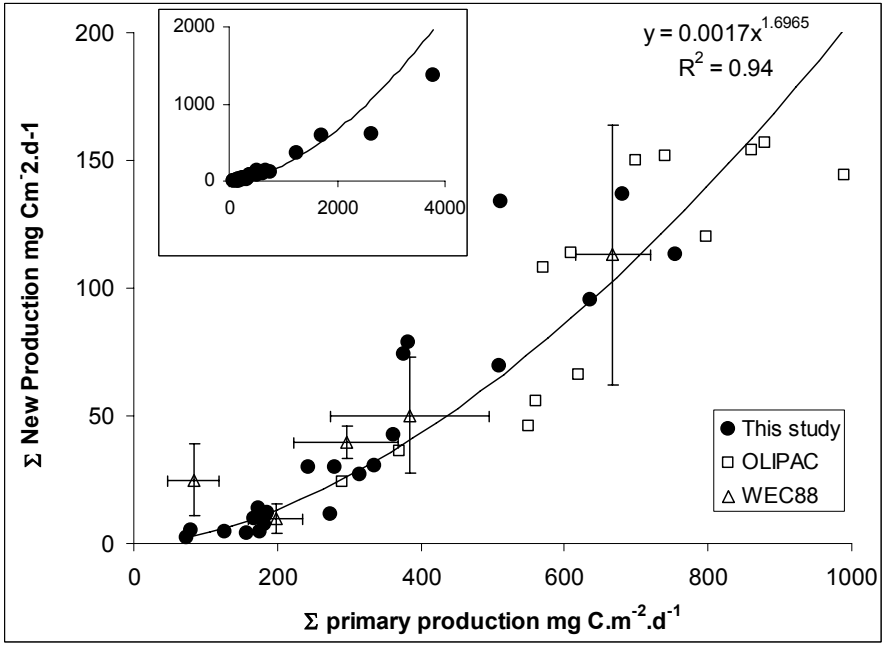

Fig. 9. Plot of integrated new production (ΣNew production) versus integrated primary production (Σprimary production). OLIPAC data are from Raimbault et al. (1999); WEC 88 data are from Dugdale et al., (1992). The power relationship is calculated from data of this study (dark points). Insert shows present data for primary production higher than 1000 mg $C.m^{-2}.d^{-1}$.

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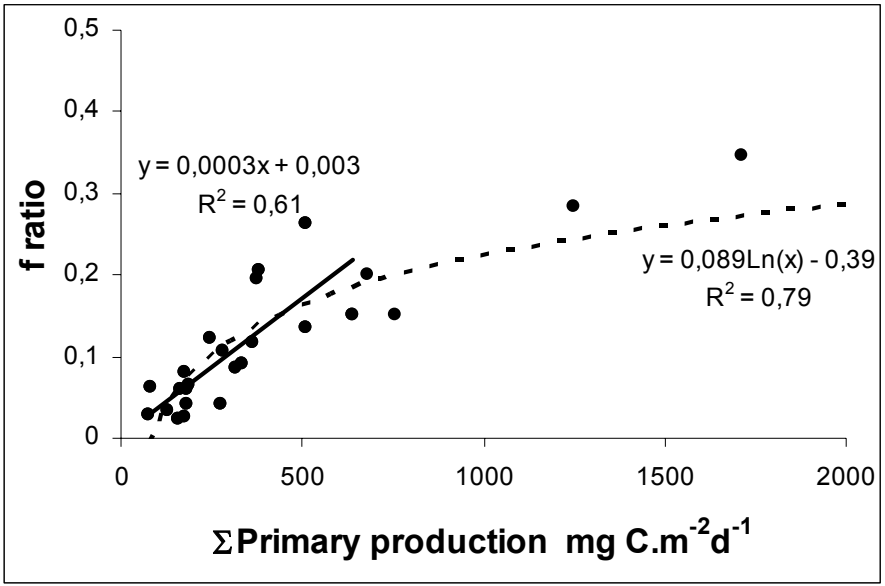

Fig. 10. Plot of mean *f* ratio (f ratio) versus integrated primary production (Σprimary production). Dashed curve is the best relationship calculated for all the data. Straight line is the linear relationship calculated for primary production lower than 500 mg $C.m^{-2}.d^{-1}$.

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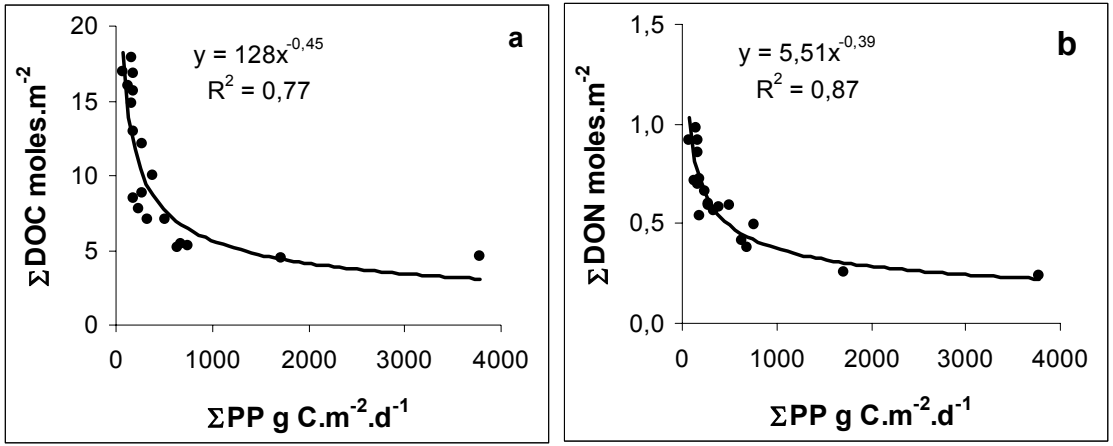

Fig. 11. Contents of dissolved organic carbon (**a**: ΣDOC) and dissolved organic nitrogen (**b**: ΣDON) over the photic layer versus integrated primary production (ΣPP).

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