
Distribution and rates of nitrogen fixation in the western tropical South Pacific Ocean constrained by nitrogen isotope budgets

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Abstract :

Constraining the rates and spatial distribution of di-nitrogen (N₂) fixation fluxes to the ocean informs our understanding of the environmental sensitivities of N₂ fixation as well as the timescale over which the fluxes of nitrogen (N) to and from the ocean may respond to each other. Here we quantify rates of N₂ fixation as well as its contribution to export production along a zonal transect in the Western Tropical South Pacific (WTSP) Ocean using N isotope ($\delta^{15}\text{N}$) budgets. Comparing measurements of water column nitrate + nitrite $\delta^{15}\text{N}$ with the $\delta^{15}\text{N}$ of sinking particulate N at a western, central, and eastern station, these $\delta^{15}\text{N}$ budgets indicate high, modest, and low rates of N₂ fixation at the respective stations. The results also imply that N₂ fixation supports exceptionally high, i.e., > 50 %, of export production at the western and central stations, which are also proximal to the largest iron sources. These geochemically-based rates of N₂ fixation are equal to or greater than those previously reported in the tropical North Atlantic, indicating that the WTSP Ocean has the capacity to support globally significant rates of N₂ fixation, which may compensate for N removal in the oxygen deficient zones of the eastern tropical Pacific.

1 Introduction

The primary source of nitrogen (N) to the ocean is the biologically-mediated reduction of di-nitrogen (N₂) gas to ammonia, which is then assimilated into the biomass of the organisms carrying out this process, known as diazotrophs (Gruber, 2004). While the distribution and rates of this process in the ocean play a central role in regulating the fertility and community structure of marine ecosystems, these first-order properties of marine N₂ fixation remain poorly constrained. Historically, the highest rates of N₂ fixation in the global ocean have been associated with the tropical North Atlantic (Mahaffey et al., 2005; Sohm et al., 2011). The high ¹⁵N₂ incubation-based N₂ fixation rates observed in the tropical Atlantic (Luo et al., 2012) are consistent with both the preference of diazotrophs for warm waters (Breitbarth et al., 2007; Stal, 2009) as well as the high atmospheric dust flux to the region (Mahowald et al., 2009; Prospero, 1996) that helps fulfil the high iron requirement of the enzyme, nitrogenase, carrying out N₂ fixation (Berman-Frank et al., 2001; Kustka et al., 2003). Additionally, the elevated ratio of nitrate (NO₃⁻) to phosphate (PO₄³⁻) concentrations (Gruber and Sarmiento, 1997) and low δ¹⁵N-NO₃⁻ (Knapp et al., 2008) in the upper thermocline of the North Atlantic are attributed to high regional N₂ fixation rates, and have supported the hypothesis that iron availability plays a key role in regulating the spatial distribution of N₂ fixation in the ocean (Moore et al., 2009; Moore and Doney, 2007) (“δ¹⁵N”, where $\delta^{15}\text{N} = \{[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}}] - 1\} * 1000$, with atmospheric N₂ as the reference).

While the highest inputs of N to the ocean have traditionally been associated with the North Atlantic, it has also been argued that this association results from the significant sampling bias in favor of the tropical Atlantic (Sohm et al., 2011), with large regions of the South Pacific and Indian Ocean under-sampled with respect to direct N₂ fixation rate measurements (Luo et al., 2012). More recently, the Eastern Tropical South Pacific (ETSP) has seen increased sampling due to nutrient distribution-based modelling predictions that the highest global N₂ fixation rates would be found in surface waters above and adjacent to oxygen deficient zones (ODZs), where significant phosphorus (P) would be available to support N₂ fixation (Deutsch et al., 2007). However, field campaigns have found exceedingly low rates of N₂ fixation in the ETSP gyre (Knapp et al., 2016a; Raimbault and Garcia, 2008) (Moutin et al.,

2008), which have been attributed to limited iron availability (Dekaezemaker et al., 2013). Consequently, existing measurements indicate that the dominant sinks for N in the ocean, benthic and water column denitrification and anaerobic ammonium oxidation, focused in the ODZs of the eastern tropical Pacific and Arabian Sea (Gruber and Galloway, 2008), are spatially segregated from the dominant N₂ fixation inputs in the tropical Atlantic. This spatial decoupling of N inputs and outputs necessarily corresponds to a temporal decoupling, requiring the time scale of ocean circulation for N₂ fixation to respond to changes in rates of denitrification, and vice versa. In spite of the apparent spatial decoupling in the modern ocean, paleoceanographic evidence indicates that N fluxes to and from the ocean have been closely balanced over ≥ 20 kya, requiring feedbacks in the N cycle to operate on time scales shorter than ocean circulation, and thus implying a tighter spatial coupling of N sources and sinks (Brandes and Devol, 2002; Deutsch et al., 2004). While N loss in the ocean is constrained to suboxic sediments and water column ODZs, similar constraints on the location of the largest N₂ fixation fluxes to the ocean are lacking, and thus the degree to which marine N sources and sinks have been coupled through time remains uncertain.

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While prior modelling analyses emphasized the importance of iron *or* phosphorus in supporting N₂ fixation, the most recent modelling studies reflect the importance of elevated surface temperatures, adequate iron, *and* the potential for low surface ocean NO₃⁻:PO₄³⁻ concentration ratios to support a unique ecological niche for diazotrophs (Dutkiewicz et al., 2012; Monteiro et al., 2011; Weber and Deutsch, 2014). Attention has consequently shifted to the relatively undersampled Western Tropical South Pacific (WTSP) Ocean, where atmospheric dust fluxes to warm surface waters are higher than in the central and eastern tropical South Pacific (Mahowald et al., 2009), and where surface ocean NO₃⁻ and PO₄³⁻ concentrations and ratios are relatively advantageous for diazotrophs (Moutin et al., 2005; Van Den Broeck et al., 2004). While seasonally some regions nearer to islands experience PO₄³⁻ drawdown to lower levels (e.g., (Van Den Broeck et al., 2004), Moutin, this issue), in parts of the WTSP gyre surface ocean NO₃⁻ concentrations are ≤ 0.1 μM and PO₄³⁻ concentrations are often ~ 0.05 to 0.2 μM (Garcia et al., 2014), with corresponding positive P* values (where $P^* = [\text{PO}_4^{3-}] - [\text{NO}_3^-]/16$) (Deutsch et al., 2007). Additionally, early remote sensing work detected significant and persistent

blooms of *Trichodesmium* spp. in the WTSP (Dupouy et al., 2000), consistent with more recent direct observations of elevated *Trichodesmium* spp. abundance and N₂ fixation rates observed near Melanesian islands (i.e., New Caledonia, Vanuatu, and Fiji) (Shiozaki et al., 2014; Yoshikawa et al., 2015) and in the Solomon Sea (Bonnet et al., 2009; 2015; Berthelot et al., 2017). These high *Trichodesmium* spp. abundances and N₂ fixation rates have been attributed to sea surface temperatures >25 °C and continuous nutrient inputs of terrigenous and volcanic origin (Labatut et al., 2014; Radic et al., 2011). Prior molecular work has also shown higher rates of N₂ fixation in the WTSP at locations where surface ocean dissolved iron (DFe) concentrations were higher and where *Trichodesmium* spp. were less stressed for iron (Chappell et al., 2012). Together, these observations and modelling-based predictions highlight the potential for significant N₂ fixation rates in regions of the WTSP where diazotrophs can meet their iron and phosphorus requirements.

Here we use geochemical tools to quantify rates of N₂ fixation along a zonal transect in the WTSP where surface waters are ≥25 °C, have favourable macronutrient concentrations and ratios, and where DFe concentrations are an order of magnitude higher than in the South Pacific Gyre, and are mainly attributable to shallow hydrothermal input (Guieu et al., under review). Specifically, we compare the δ¹⁵N of the two dominant sources of “new” N to surface waters, subsurface NO₃⁻ and N₂ fixation, with the δ¹⁵N of the sinking particulate N (PN_{sink}) flux to estimate the relative importance of both NO₃⁻ and N₂ fixation as a source of new N to surface waters. This approach relies on subsurface NO₃⁻ and N₂ fixation having distinct isotopic compositions. N₂ fixation introduces new N to the ocean with a δ¹⁵N of ~ -1‰ (Carpenter et al., 1997; Hoering and Ford, 1960; Minagawa and Wada, 1986). In contrast, in the Pacific, NO₃⁻ mixed up from the subsurface is impacted by water column denitrification and can have a NO₃⁻ δ¹⁵N >20‰ (e.g., (Brandes et al., 1998; Casciotti et al., 2013; Rafter and Sigman, 2016)), although as upper thermocline waters move westward in the Pacific, the very high NO₃⁻ δ¹⁵N signal is diluted and typical values are between 5 and 10‰ (Rafter et al., 2013). The relative importance of each source for supporting export production can be determined using the two end-member mixing model described in Eqn. 1 (“δ¹⁵N budget”) where the fractional importance of N₂ fixation for supporting export production (x) is defined as:

$$PN_{\text{sink}} \delta^{15}\text{N} = x(-1\text{‰}) + (1 - x)(\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}) \quad \text{Eq. 1}$$

Rearranging and solving for x yields:

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$$x = (\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N} - PN_{\text{sink}} \delta^{15}\text{N}) / (1 + \text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}) \quad \text{Eq. 2}$$

Multiplying the fraction of export production supported by N_2 fixation (x) by the PN_{sink} mass flux provides a time-integrated N_2 fixation rate that can be compared with $^{15}\text{N}_2$ incubation-based N_2 fixation rate measurements (Knapp et al., 2016a). Here it is hypothesized that both rates of N_2 fixation and its importance for fuelling export production will be higher at stations in the western vs. central and eastern regions of the WTSP because of their closer proximity to iron sources (Guieu et al., under review).

2 Methods

2.1 Sample collection

15 Sampling for the Oligotrophic to Utra-oligotrophic PACific Experiment (“OUTPACE”) cruise was conducted on the R/V L’Atalante, which left Noumea, New Caledonia on 18 February 2015 and arrived in Papeete, Tahiti, on 2 April 2015. This cruise followed a roughly zonal transect along 18 to 19 °S between 159 °E and 160 °W. Details of the cruise and experimental design are described comprehensively in (Moutin et al., 2017), but briefly, sediment traps were deployed at three “Long Duration” (LD) stations A, B, and C (see Table 1 for station locations). Water column samples were collected from Niskin bottles deployed on a CTD-rosette and water was stored at -20 °C in HDPE bottles for analysis on land.

2.2 $\text{NO}_3^- + \text{NO}_2^-$ concentration and $\delta^{15}\text{N}$ measurements

25 The concentrations of $\text{NO}_3^- + \text{NO}_2^-$ in water column samples collected on the OUTPACE cruise were measured by colorimetric methods (Aminot and Kerouel, 2007). The $\delta^{15}\text{N}$ of $\text{NO}_3^- + \text{NO}_2^-$ in samples collected on the OUTPACE cruise was measured using the denitrifier method (Casciotti et al., 2002;

Sigman et al., 2001), with modifications (McIlvin and Casciotti, 2011). Typical standard deviation of the $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ analyses was $\pm 0.4\%$.

2.3 Sinking particulate N flux and $\delta^{15}\text{N}$ measurements

Surface-tethered floating particle-interceptor traps (PPS5) were deployed on the OUTPACE cruise at 5 150, 330 and 520 m for ~ 5 days at Stations LDA and LDB, and at 150 and 330 m at LDC (Moutin et al., 2017). The mass flux (“ PN_{sink} flux”) and $\delta^{15}\text{N}$ of the PN_{sink} flux was determined by combustion-GC interfaced to an isotope ratio mass spectrometer at the Mediterranean Institution of Oceanography with a lower detection limit of $2.2 \mu\text{g N}$ and precision of $\pm 0.3\%$ for $80 \mu\text{g}$ samples, with a precision of $\pm 1.0\%$ for 10 to $20 \mu\text{g}$ samples typical of what was collected in the sediment traps at the LD stations.

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3 Results

3.1 $\text{NO}_3^- + \text{NO}_2^-$ concentration and $\delta^{15}\text{N}$, and $\text{PN}_{\text{sink}} \delta^{15}\text{N}$

Samples collected in the upper 70 m at the LD stations had $\leq 0.1 \mu\text{M}$ $\text{NO}_3^- + \text{NO}_2^-$ (Caffin et al., 2017) and increased with depth, consistent with prior regional observations (Garcia et al., 2014) (Fig. 1). All 15 nutrient concentration data are available at: <http://www.obs-vlfr.fr/proof/php/outpace/outpace.php>. Water column profiles of thermocline $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ show similar trends at the LD stations, with 650 m $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N} \sim 7\%$, increasing to $\sim 8.5\%$ at 400 m (Fig. 1), which fall within the range of previous regional measurements (Yoshikawa et al., 2015). The elevation of thermocline $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ relative to the mean ocean $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ of 5% is attributed to denitrification and/or anammox occurring in 20 the ODZs of the ETSP, where thermocline $\text{NO}_3^- \delta^{15}\text{N}$ can exceed 20% (e.g., (Altabet et al., 2012; Casciotti et al., 2013)). The average, mass-weighted $\delta^{15}\text{N}$ of the PN_{sink} flux collected in the 150 m trap increased from the western to eastern stations, from $0.6 \pm 1.0\%$ at LDA, to $3.1 \pm 1.0\%$ at LDB, and to $7.7 \pm 1.0\%$ at LDC (Table 1) (Fig. 1).

3.2 Results of the $\delta^{15}\text{N}$ budget: N_2 fixation rates and their contribution to export production

25 Estimates of N_2 fixation rates and their contribution to export production determined using $\delta^{15}\text{N}$ budgets include the quantitatively dominant fluxes of N into and out of the surface ocean. Here, the dominant

fluxes of N into the surface ocean include subsurface NO_3^- and newly fixed N introduced from diazotrophs, and the dominant loss term is represented by the PN_{sink} flux (Eq. 1). In the event that total dissolved N (TDN) concentrations vary in space/time, they may be included as well, however, surface ocean TDN concentrations from the OUTPACE cruise show little to no zonal gradient, and were typically between 5 and 7 μM in the upper 100 m (Moutin et al., This issue), and so are not included in $\delta^{15}\text{N}$ budget calculations. Additionally, the importance of N in atmospheric deposition has recently received significant attention, especially in the northwest Pacific (e.g., (Kim et al., 2014)), raising the possibility that atmospheric N deposition might also be an important source of N in the WTSP. However, the atmospheric N deposition flux measured on the OUTPACE cruise, 0.2 $\mu\text{mol N m}^{-2} \text{d}^{-1}$ (Caffin et al., 2017), is several orders of magnitude lower than the mass flux captured in the 150 m sediment traps, 30 to 300 $\mu\text{mol N m}^{-2} \text{d}^{-1}$ (Table 1), indicating that atmospheric N deposition is an insignificant source of new N to regional surface waters, and so is neglected in our $\delta^{15}\text{N}$ budget calculations.

While gradients with depth in subsurface $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ at the OUTPACE LD stations are modest compared to those in the ETSP, due to the relatively low sampling resolution in the upper thermocline where NO_3^- is likely sourced, we calculate $\delta^{15}\text{N}$ budgets using a range of $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ end-member values, which are represented by the shaded regions in Fig. 1. At each LD station, the $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ lower bound is represented by the 650 m sample and the upper bound is represented by the 400 m sample. Samples collected shallower than this (i.e., ≤ 200 m) show elevation in $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ as the $\text{NO}_3^- + \text{NO}_2^-$ concentration decreases, and reflects the effect of NO_3^- assimilation, as is commonly observed below the euphotic zone in other oligotrophic regions (Knapp et al., 2016a; Knapp et al., 2008), and thus do not represent the $\delta^{15}\text{N}$ of the source NO_3^- . Using the $\text{PN}_{\text{sink}} \delta^{15}\text{N}$ ($\pm 1\%$ 1 S.D.) and the range in subsurface $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ end-member values in Eq. 2 corresponds to 80 to 83 $\pm 13\%$, 50 to 57 $\pm 12\%$, and 0 to 8 $\pm 11\%$ of export production supported by N_2 fixation at stations LDA, LDB, and LDC, respectively (Table 1). Multiplying the fractional importance of N_2 fixation by the PN_{sink} mass flux yields a range of estimated N_2 fixation rates of 219 to 290, 11 to 21, and 0 to 9 $\mu\text{mol N m}^{-2} \text{d}^{-1}$ at

stations LDA, LDB, and LDC, respectively (Table 1), where the range includes uncertainty in both the $\text{PN}_{\text{sink}} \delta^{15}\text{N}$ measurement as well as the $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ end-member.

These geochemically-derived rates are lower than those measured by *in situ* $^{15}\text{N}_2$ incubations at the same OUTPACE stations, with depth-integrated average N_2 fixation rates of 593 ± 51 , 706 ± 302 , and $59 \pm 16 \mu\text{mol N m}^{-2} \text{d}^{-1}$ at LDA, LDB, and LDC, respectively (Caffin et al., 2017). Previous work has also found lower $\delta^{15}\text{N}$ budget-derived N_2 fixation rates relative to $^{15}\text{N}_2$ incubation-based N_2 fixation rates (Knapp et al., 2016a). To the extent that sediment traps under collect the export flux, the two different metrics of N_2 fixation may be reconciled by multiplying “x” from Eq. 2, the fractional importance of N_2 fixation for export production, by other metrics of new or export production such as O_2/Ar ratios, ^{234}Th deficits, or ^{14}C uptake rates (Knapp et al., 2016a). This explanation may reconcile the $\delta^{15}\text{N}$ budget and $^{15}\text{N}_2$ incubation-based N_2 fixation rate estimates at LDA, which differ by a factor of ~ 2.5 , and potentially the rates at LDC as well, which, while they differ by a factor ≥ 6 , both correspond to relatively low N_2 fixation rates. However, the $\delta^{15}\text{N}$ budget and $^{15}\text{N}_2$ incubation-based N_2 fixation rates observed at LDB, 11 to 21 and $706 \mu\text{mol N m}^{-2} \text{d}^{-1}$, respectively, are more difficult to reconcile based on sediment trap under-collection alone, and may be partially attributable to variability encountered while sampling at the end of a phytoplankton bloom at that station (de Verneil et al., 2017). We note that the zonal trend in increasing $\text{PN}_{\text{sink}} \delta^{15}\text{N}$ to the east is similar to a zonal gradient in suspended particulate N ($\text{PN}_{\text{susp}} \delta^{15}\text{N}$) (Bonnet et al., This Issue), suggesting that the $\delta^{15}\text{N}$ of the PN_{sink} observed at LDB is consistent with other regional geochemical data. Additionally, the $^{15}\text{N}_2$ incubation-based N_2 fixation rate at LDB has relatively large error bars, resulting from observations of decreasing *in situ* N_2 fixation rates over the course of several daily observations at LDB (Caffin et al., 2017), which may also contribute to the offset between the $^{15}\text{N}_2$ incubation and $\delta^{15}\text{N}$ budget-based N_2 fixation rate estimates. Further, the PN_{sink} flux collected in the 150 m trap at LDB, $0.030 \text{ mmol N m}^{-2} \text{d}^{-1}$, was somewhat lower than the PN_{sink} flux collected in the 330 and 520 m traps at the same station, 0.034 and $0.036 \text{ mmol N m}^{-2} \text{d}^{-1}$, respectively, which is unexpected given the more typical mass flux attenuation with depth observed at LDA and LDC, as well as elsewhere in the ocean (Martin et al., 1987). This unusual trend in mass flux with depth suggests either non-steady state sinking flux conditions and/or a

problem with sample collection at LDB. Regardless, using the ^{14}C -uptake based estimate of net community production at LDB, $1.91 \text{ mmol N m}^{-2} \text{ d}^{-1}$, instead of the PN_{sink} mass flux to multiply “x” from Eq. 2 by yields an N_2 fixation rate of $2300 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$. These significant disparities in productivity metrics and resulting N_2 fixation rates at LDB suggests the potential for temporal decoupling of production and export and/or the underestimation of the export flux by the sediment trap, and indicate that N_2 fixation rates are probably higher than those resulting from $\delta^{15}\text{N}$ budget calculations based on the mass flux to the 150 m trap at LDB. Regardless, we take the zonal trend in $\text{PN}_{\text{sink}} \delta^{15}\text{N}$ to indicate a decreasing contribution from N_2 fixation to export from the west to the east to be robust as it is consistent with both the $\text{PN}_{\text{susp}} \delta^{15}\text{N}$ measurements as well as the broad trends in $^{15}\text{N}_2$ incubation-based N_2 fixation rate estimates that decrease from the west to east.

Comparing the absolute magnitude of the $\delta^{15}\text{N}$ budget-based N_2 fixation rates with previous measurements, we find that the 219 to $290 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$ rate estimated for LDA represents a significant N_2 fixation rate relative to prior global measurements (Luo et al., 2012), in particular if it should be revised upwards to account for the under-collection of the export flux by the sediment trap. In contrast, the estimated rate range at LDB, 11 to $21 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$, is quite low, as is the range of 0 to $9 \text{ } \mu\text{mol N m}^{-2} \text{ d}^{-1}$ at LDC, and both of these rates are broadly similar to the rates previously measured in the ETSP (Knapp et al., 2016a; Moutin et al., 2008; Raimbault and Garcia, 2008). Similarly, the $\delta^{15}\text{N}$ -budget based estimate of the contribution of N_2 fixation to export production at LDC is low and similar to previous $\delta^{15}\text{N}$ -budget measurements in the North Pacific (Casciotti et al., 2008) and North Atlantic (Altabet, 1988; Knapp et al., 2005). However, the fractional contribution of N_2 fixation to export production at LDA, 80 to 83%, is higher than all previous $\delta^{15}\text{N}$ budget results. The contribution of N_2 fixation to export production at LDB, 50 to 57%, is also notably high. While the previous $\delta^{15}\text{N}$ budgets of (Karl et al., 1997) and (Dore et al., 2002) found evidence for ~50% of export production supported by N_2 fixation near Hawaii, newer methods capable of measuring the $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ at the lower $\text{NO}_3^- + \text{NO}_2^-$ concentrations found in the upper thermocline that represent a more realistic estimate of the end-member NO_3^- source suggest that N_2 fixation may support closer to 25% of export during the summer in the North Pacific gyre (Bottjer et al., 2017; Casciotti et al., 2008). Consequently, the findings of 50 to

57% and 80 to 83% of export production being supported by N_2 fixation at stations LDB and LDA, respectively, indicates that N_2 fixation plays a significant role supporting carbon fixation and export production in this region of the WTSP, consistent with the high e-ratios (up to 9.7) reported by (Caffin et al., 2017). Direct export of diazotrophs has been reported by (Caffin et al., 2017), but most export is likely indirect, i.e., after the transfer of diazotroph-derived N to non-diazotrophic plankton, that is subsequently exported (Caffin et al., This issue), as has been observed elsewhere in the WTSP (Bonnet et al., 2016; Knapp et al., 2016b).

4 Discussion

4.1 Environmental sensitivities of N_2 fixation and the basin-scale coupling of N sources and sinks

10 The zonal gradient in both N_2 fixation rates as well as their contribution to export production in the OUTPACE study supports emerging hypotheses regarding the controls on the distribution of marine N_2 fixation fluxes in the global ocean. Specifically, the low rates of N_2 fixation documented in this study at LDC and in the ETSP (Knapp et al., 2016a) indicate that low $NO_3^-:PO_4^{3-}$ concentration ratios in the absence of adequate iron (Blain et al., 2008; Fitzsimmons et al., 2014) are insufficient to support
15 significant fluxes of new N to the ocean. Instead, the results presented here are consistent with recent modelling work that has included *both* the high iron requirements of diazotrophs as well as the potential for low $NO_3^-:PO_4^{3-}$ concentration ratios to support elevated diazotroph abundance and N_2 fixation inputs to the ocean (Dutkiewicz et al., 2012; Monteiro et al., 2011; Weber and Deutsch, 2014). Indeed, these new modelling efforts have identified the WTSP as a unique region where PO_4^{3-} concentrations are
20 relatively high, NO_3^- concentrations are low, and atmospheric dust fluxes provide a moderate source of iron to warm surface waters, conditions seemingly favourable for significant N_2 fixation fluxes. While regions within the WTSP nearer to islands experience significant PO_4^{3-} drawdown, with seasonal PO_4^{3-} turnover times comparable to those observed in the Sargasso Sea (Van Den Broeck et al., 2004; Van Mooy et al., 2009), these modelling predictions are supported by recent reports of high regional $^{15}N_2$
25 incubation-based N_2 fixation rates (Bonnet et al., 2017).

However, prior to the OUTPACE cruise, our knowledge of DFe concentrations and their sources in the WTSP was limited, especially in the western and central sectors. During OUTPACE, Guieu et al. (Under review) reported high DFe concentrations in the western sector of the WTSP (from 160 °E to 165 °W, average 1.7 nM within the photic layer), i.e., significantly ($p < 0.05$) higher than those reported in the eastern sector (165 °W to 160 °W, average 0.3 nM within the photic layer). The high DFe concentrations measured in the west were previously undocumented, and reveal several maxima (> 50 nM), suggesting significant iron inputs to this region. (Guieu et al., Under review) found that atmospheric deposition in this region was too low to explain the observed DFe concentrations in the water column, and that the iron in the euphotic layer may instead derive from shallow (~ 500 m) hydrothermal sources associated with the Tonga-Kermadec subduction zone.

Recent studies performed in the western end of the WTSP in the Solomon, Bismarck (Berthelot et al., 2017; Bonnet et al., 2009; Bonnet et al., 2015) and Arafura (Messer et al., 2015; Montoya et al., 2004) Seas also reveal extremely high N_2 fixation rates ($> 600 \mu\text{mol N m}^{-2} \text{d}^{-1}$), indicating that high N_2 fixation rates have been found over a significant region of the WTSP, extending west to east from Australia to Tonga and north to south from the equator to 25 to 30 °S, or $\sim 13 \times 10^6 \text{ km}^2$ (i.e. ~ 20 % of the South Pacific Ocean area). These significant N inputs may offset the N loss occurring in the ODZs of the eastern tropical Pacific. The ability for marine N inputs and outputs to compensate for each other within the same ocean basin corresponds to a spatial and thus temporal coupling on the scale of years to decades, consistent with the paleoceanographic record (Brandes and Devol, 2002; Deutsch et al., 2004; Weber and Deutsch, 2014), and represents an intermediate view of the distribution of global marine N_2 fixation fluxes consistent with that proposed by (Weber and Deutsch, 2014) where iron availability controls local N_2 fixation rates but phosphorus availability regulates basin-scale N_2 fixation rates (Moutin et al., 2008 and this issue).

5 Conclusions

The goal of this study was to address the question: do regions other than the tropical Atlantic contribute significantly to global N_2 fixation fluxes? While our results should be taken as a “snapshot” view that cannot necessarily be scaled up to annual fluxes, at stations proximal to iron sources, geochemically-

derived N_2 fixation rates of 219 to 290 $\mu\text{mol N m}^{-2} \text{d}^{-1}$ were observed, and could potentially represent a lower bound of N_2 fixation rates due to the potential under-collection of the PN_{sink} flux by sediment traps. Moreover, at stations LDA and LDB, separated by $\sim 27^\circ$ longitude, N_2 fixation was found to support $>50\%$ of export production, a finding that has not been replicated elsewhere with sensitive $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ methods to our knowledge. Together with similar findings from $^{15}\text{N}_2$ uptake experiments, these results suggests that N_2 fixation can support a significant fraction of export production over a large region of the WTSP. At the eastern station most distant from iron sources, both rates and the contribution of N_2 fixation to export production were low, ~ 0 to 9 $\mu\text{mol N m}^{-2} \text{d}^{-1}$ and 0 to 8%, respectively, similar to previous measurements in the ETSP where diazotrophs may also be challenged by iron availability (Dekaezemacker et al., 2013; Knapp et al., 2016a; Moutin et al., 2008). Significant N_2 fixation fluxes in the WTSP may provide a means of balancing N loss occurring in the ODZs of the eastern tropical Pacific, and thus may help reconcile the paleoceanographic record requiring N inputs and losses to balance each other on time scales shorter than ocean circulation (Dutkiewicz et al., 2012; Monteiro et al., 2011; Weber and Deutsch, 2014).

15 **Acknowledgments, Samples, and Data**

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25 All data and metadata are available at the following web address: <http://www.obs-vlfr.fr/proof/php/outpace/outpace.php>. The data supporting the conclusions of this paper may be obtained at the BCO-DMO database (# Pending), as well as the CCHDO site:

<https://cchdo.ucsd.edu/cruise/320620170820>. The authors declare no other affiliations or real or perceived financial conflicts of interest with respect to the results of this paper.

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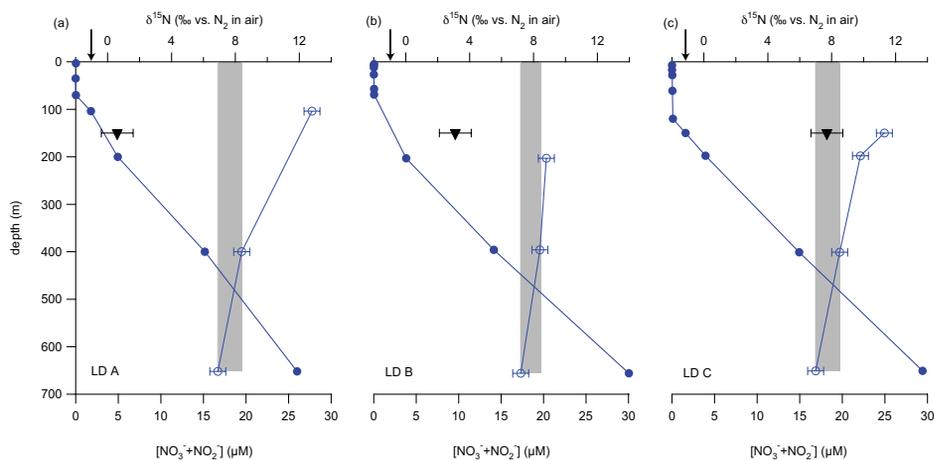


Figure 1. $\text{NO}_3^- + \text{NO}_2^-$ concentration (filled circles), $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ (open circles), and $\text{PN}_{\text{sink}} \delta^{15}\text{N}$ (filled inverted triangles) from OUTPACE “long duration” (LD) stations A (a), B (b), and C (c). Error bars represent 1 standard deviation, and are smaller than symbol size for $\text{NO}_3^- + \text{NO}_2^-$ concentration. The range of $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ end-member values used for $\delta^{15}\text{N}$ budget calculations are represented by shaded regions. The N_2 fixation end-member $\delta^{15}\text{N}$ value, -1‰ , is represented by the arrow on the upper x-axis.

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Table 1. Location, subsurface $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$, $\text{PN}_{\text{sink}} \delta^{15}\text{N}$, and N_2 fixation rate and contribution to export at the OUTPACE long duration stations.

Station	Latitude ($^{\circ}\text{N}$)	Longitude ($^{\circ}\text{E}$)	Average PN_{sink} flux ($\text{mmol N m}^{-2} \text{d}^{-1}$)	$\text{PN}_{\text{sink}} \delta^{15}\text{N}^*$ (‰)	150 m Trap Subsurface $\text{NO}_3^- + \text{NO}_2^- \delta^{15}\text{N}$ (‰)	% Export	N_2 fixation rate ($\mu\text{mol N m}^{-2} \text{d}^{-1}$)
LDA	-19.22	163.59	0.303	0.6 ± 1	6.9 to 8.4	80 to $83 \pm 13\%$	219 to 290
LDB	-18.18	-170.74	0.03	3.1 ± 1	7.2 to 8.4	50 to $57 \pm 12\%$	11 to 21
LDC	-18.5	-165.79	0.047	7.7 ± 1	7.0 to 8.5	0 to $8 \pm 11\%$	0 to 9

*Flux-weighted mean $\text{PN}_{\text{sink}} \delta^{15}\text{N}$