Nitrogen Isotope Simulations Confirm the Importance of Atmospheric Iron Deposition for Nitrogen Fixation Across the Pacific Ocean

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Abstract

Nitrogen (N) fixation by specialized microorganisms (diazotrophs) influences global plankton productivity because it provides the ocean with most of its bio-available N. However, its global rate and large-scale spatial distribution is still regarded with considerable uncertainty. Here we use a global ocean nitrogen isotope model, in comparison with $\delta^{15}NO_3^-$ observations, to constrain the pattern of N_2 fixation across the Pacific Ocean. N_2 fixation introduces isotopically light atmospheric N_2 from to the ocean ($\delta^{15}N = 0‰$) relative to the oceanic average near 5‰, which makes nitrogen isotopes suitable to infer patterns of N_2 fixation. Including atmospheric iron limitation of diazotrophy in the model shifts the pattern of simulated N_2 fixation from the South Pacific to the North Pacific and from the East Pacific westward. These changes considerably improve the agreement with meridional transects of available $\delta^{15}NO_3^-$ observations, as well as excess P ($PO_4^{3-} - NO_3^-/16$), confirming that atmospheric iron deposition is indeed important for N fixation in the Pacific Ocean. This study highlights the potential for using $\delta^{15}N$ observations and model simulations to constrain patterns and rates of N fixation in the ocean.

1. Introduction

Nitrogen (N) fixation is regarded as the dominant source of biologically available nitrogen (fixed-N) into the ocean [*Codispoti*, 2007], which is performed by specialized prokaryotes (diazotrophs) that are capable of reducing N_2 gas instead of forms of oceanic fixed-N (NO_3^-, NO_2^-, NH_4^+) during photosynthesis. Since diazotrophs are not limited by fixed-N, they can grow in N-depleted surface water provided other required nutrients (e.g., phosphorus (P) and iron (Fe)) are available for uptake. Diazotrophs can have an important influence on climate because fixed-N limits primary production and biological sequestration of atmospheric CO_2. The large spatial and temporal variability of diazotrophs makes it difficult to constrain the global rate of N_2 fixation. Recent estimates of N_2 fixation have seen upward revisions, but still range widely between ~100 – 200 Tg N yr^{-1} [*Gruber and Sarmiento,* 1997; *Karl et al.,* 2002; *Deutsch et al.*, 2007; *Moore and Doney*, 2007]. The efficiency, with which diazotrophs can balance the N-loss from denitrification and anammox, the major sinks for fixed-N, largely determines if the oceanic fixed-N inventory could fluctuate significantly enough to affect atmospheric CO_2 through changes in the biological pump.

Throughout much of the contemporary ocean, biological productivity is limited by fixed-N suggesting other factors are preventing diazotrophs from fixing N, such as light, temperature, and/or P and Fe availability. It follows that blooms of *Trichodesmium*, one of the most important and best studied diazotrophs, occur more frequently and are more extensive in warm (>25°C) surface water where rates of atmospheric Fe deposition are high such as the North Atlantic, Indian, and North Pacific compared to areas of low Fe deposition such as the South Pacific where the abundance of *Trichodesmium* appears to be much lower [*Carpenter*, 1983; *Karl et al.*, 2002; *Carpenter and Capone*, 2008]. This suggests that temperature and Fe availability may be

51 the most important factors that determine where N_2 fixation is able to occur. However, other
52 more uncharacterized unicellular diazotrophs have been observed to grow in cooler water near
53 20°C [*Needoba et al.*, 2007], and it has been suggested that they also may significantly
54 contribute to the global N_2 fixation rate [*Zehr et al.*, 2001; *Montoya et al.*, 2004].

55 N_2 fixation introduces relatively isotopically light N ($\delta^{15}N = 0‰$) into the ocean
56 compared to the global mean $\delta^{15}NO_3^-$ near 5‰. Therefore, the ratio of the two stable nitrogen
57 isotopes, represented in the $\delta^{15}N$ notation where $\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{atmosphere} -$
58 1]•1000, may be a powerful tool to trace patterns of N_2 fixation. We will compare a model of
59 nitrogen isotopes, embedded within the ocean component of a global Earth System Climate
60 Model, with $\delta^{15}NO_3^-$ measurements across the Pacific Ocean to constrain N_2 fixation. We focus
61 on the effect of atmospheric Fe limitation of diazotrophy.

62 **2. Model Description**

63 **2.1 Marine Ecosystem/Biogeochemical Model**

64 The marine ecosystem/biogeochemical model is the NPZD (Nutrient, Phytoplankton,
65 Zooplankton, Detritus) ecosystem model of *Somes et al.*, [2010]. The organic variables include
66 two classes of phytoplankton, diazotrophs (P_D), which can undergo N_2 fixation (Figure 1), and a
67 "general" NO_3^- assimilating phytoplankton class (P_G), as well as zooplankton (Z) and organic
68 detritus (D). The inorganic variables include dissolved oxygen (O_2) and two nutrients, nitrate
69 (NO_3^-) and phosphate (PO_4^{3-}), both of which are consumed by phytoplankton and remineralized
70 in fixed elemental ratios ($R_{N:P} = 16$, $R_{O:P} = 170$). We note, though, that diazotrophs have been
71 found to have $R_{N:P}$ as high as 50:1 (e.g., *Letelier and Karl*, [1996; 1998]). This simplification is
72 one of the reasons why excess phosphorus, $xsP = PO_4^{3-} - NO_3^-/16$, is generally overestimated
73 near the surface in the model (Figure 2). Denitrification, the replacement of O_2 with NO_3^- as the

electron acceptor during the respiration of organic matter, occurs under suboxic conditions (O_2 < 5 μM) in the water column and the sea floor sediments [*Codispoti and Richards*, 1976] . Since the model underestimates coastal upwelling (due to its coarse resolution), which drives large fluxes of organic carbon to the sea floor that create suboxic conditions in the sediments, the benthic denitrification parameterization [*Middleburg et al.*, 1996] is tuned to set the global mean $\delta^{15}NO_3^-$ to observations near 5‰ by multiplying this parameterization by a constant factor (α_{SD} = 8) (see *Somes et al.*, [2010]).

Diazotrophs grow according to the same principles as general phytoplankton in the model, but we also account for some of their different characteristics. N_2 fixation breaks down the triple-N bond of N_2, which is energetically more costly than assimilating fixed-N. Therefore, in the model, the growth rate of diazotrophs is lower than that of general phytoplankton. It is zero in waters cooler than 15°C and increases 40% slower with temperature than the growth rate of general phytoplankton. Diazotrophs are not limited by NO_3^- and can out-compete general phytoplankton in surface waters that are depleted in fixed-N, but still contain sufficient P (i.e., high xsP water due to denitrification). However, diazotrophs will consume NO_3^- if it is available, consistent with culture experiments [*Mulholland et al.*, 2001; *Holl and Montoya*, 2005], which is another factor that inhibits N_2 fixation in the model. Denitrification, and the propagation of N-deficient waters into the shallow thermocline by physical transport processes, creates an ecological niche for diazotrophs in the model, which stimulates N_2 fixation [*Tyrrell*, 1999]. Fe is currently not included as a prognostic tracer in the model. However, we include a simple parameterization of atmospheric Fe limitation of diazotrophy as described in Section 3.

2.2 Nitrogen Isotope Model

The nitrogen isotope model simulates the distribution of the two stable nitrogen isotopes, ^{14}N and ^{15}N, in all N species included in the marine ecosystem model. The processes in the model that fractionate nitrogen isotopes are algal NO_3^- assimilation (ε_{ASSIM} = 5‰), zooplankton excretion (ε_{EXCR} = 6‰), water column denitrification (ε_{WCD} = 25‰), and N_2 fixation (ε_{NFIX} = 1.5‰). Fractionation results in the isotopic enrichment of the more reactive, thermodynamically preferred, light ^{14}N into the product of each reaction by a process-specific fractionation factor. For a detailed discussion of nitrogen isotope fractionation dynamics see [*Mariotti et al.,* 1981]. Although little fractionation occurs during N_2 fixation in the model, it has an important effect on $\delta^{15}N$ by introducing isotopically light atmospheric N_2 ($\delta^{15}N$ = 0‰) into the oceanic fixed-N pool. Benthic denitrification has been observed to have little effect on the oceanic isotopic N pool because denitrifiers consume nearly all NO_3^- diffusing into the reactive zones within the sediments, leaving the oceanic N pool mostly unaltered [*Brandes and Devol*, 2002; *Lehmann et al.*, 2004; *Lehmann et al.*, 2007]. Therefore, in the model, there is no fractionation during benthic denitrification (ε_{BD} = 0‰), although this is a simplification of observations [*Lehmann et al.*, 2007]. Fractionation during the remineralization of organic matter to NO_3^- is not included in the model. The complete nitrogen isotope model description is provided in *Somes et al.*, [2010].

3. Atmospheric Fe Limitation of Diazotrophy

The nitrogenase enzyme, which fixes N_2 in diazotrophs, has a large structural iron (Fe) requirement [*Raven*, 1988; *Sanudo-Wilhelmy et al.*, 2001]. Diazotrophs may depend on Fe from atmospheric deposition in oligotrophic waters, where a deep pycnocline inhibits upward mixing of subsurface Fe-replete waters into the euphotic zone. Therefore, we include an atmospheric Fe limitation of diazotrophy experiment (FeLim), where diazotrophs' growth rate is further reduced

by the Fe limitation parameter (*FeL*), which scales an estimate of monthly climatolgoical atmospheric dust deposition [*Mahowald et al.*, 2005] between 0 and 1 (Figure 1) by multiplying atmospheric dust deposition rate by a constant factor, and setting the maximum value to 1 (i.e., maximum growth rate = μ_D•*FeL*). We note that the model still does not account for any Fe input from rivers or shelf sediments.

3. Results

The control (CTL) simulation does not include any Fe limitation of diazotrophs (i.e., maximum growth rate = μ_D) and results in large N_2 fixation rates in the Central and Eastern Tropical South Pacific (Figure 1). The only factor that prevents N_2 fixation from occurring in the Eastern Tropical Pacific of CTL is the presence of high surface NO_3^- in the core of the HNLC region, where diazotrophs will consume NO_3^- instead of fixing dissolved N_2 to meet their N requirement for growth. This pattern of tight coupling of N_2 fixation and denitrification in the Eastern Tropical South Pacific is consistent with the model of *Deutsch et al.*, [2007], which predicts N_2 fixation based on the xsP distribution in a general ocean circulation model, but does not include any Fe limitation or NO_3^- inhibition.

Considering atmospheric Fe limitation of diazotrophs (FeLim), the pattern of N_2 fixation —such as high values in the tropical/subtropical North Pacific, the western tropical/subtropical South Pacific, the western tropical/subtropical South Atlantic, the tropical/subtropical North Atlantic and the Indian Ocean—is much more consistent with direct observations (e.g., *Karl et al.*, [2002]; *Carpenter and Capone*, [2008]), and with results from a more complex ecosystem/biogeochemical model [*Moore and Doney*, 2007]. However, N_2 fixation in our model does not extend northward of ~30°N in the North Pacific, whereas some observations show N_2 fixation as far north as 35–40°N [*Church et al.*, 2008; *Kitajima et al.*, 2009]. We hypothesize

this discrepancy occurs due to the oversimplified fast-recycling microbial loop parameterization, which recycles organic matter to inorganic nutrients at N:P=16. It has been suggested that P recycles more efficiently relative to N through these microbial loops [*Wu et al.*, 2000], which is a mechanism that could help relieve diazotrophs of their P limitation throughout the tropical/subtropical oligotrophic ocean and stimulate additional N_2 fixation.

Global measures of $\delta^{15}NO_3^-$ and xsP improve in FeLim compared to CTL (Table 1). Generally lower $\delta^{15}NO_3^-$ and xsP in the Northern Hemisphere relative to the Southern Hemisphere in FeLim, due to more N_2 fixation occurring in the Northern Hemisphere where more atmospheric Fe deposition exists, result in a better match with observations than in CTL (Figure 2). The Central and Western Tropical Pacific are both "downstream" from the suboxic zones in the Eastern Pacific, representing potential regions where N_2 fixation may occur as high xsP flows westward out of the Eastern Pacific denitrification zones. Measured $\delta^{15}NO_3^-$ shows a decreasing trend northwards in the two transects across the Pacific (Figure 3), with a minimum near the equator in the Central Pacific transect. This equatorial minimum is reproduced in the model due to the low degree of surface NO_3^- utilization as a result of extensive NO_3^- supply to the surface from equatorial upwelling. The northward decreasing $\delta^{15}NO_3^-$ trend in FeLim in both transects is due to more N_2 fixation occurring north of the equator, where sufficient atmospheric Fe deposition exists (Figure 1). When atmospheric Fe limitation of diazotrophy is not included in the model (CTL), the opposite $\delta^{15}NO_3^-$ trend is simulated because more N_2 fixation occurs south of the equator, in contrast to the observations.

4. Discussion

We have highlighted two affects that can prevent N_2 fixation in the Pacific: Fe limitation and NO_3^- inhibition. Nitrate contours in World Ocean Atlas 2005 (WOA) show the potential effect of NO_3^- inhibition on N_2 fixation. xsP is generally not restored close to 0 (~0.1 - 0.2 μM) until near-surface (0 – 100 m) NO_3^- is almost completely consumed in the Western Pacific (see 0.5 μM NO_3^- contour, Figure 2), but xsP remains high (> ~0.4 μM) where large near-surface NO_3^- concentrations exist in the Eastern Pacific (see 5.0 μM NO_3^- contour, Figure 2). A meridional gradient in the Western Tropical Pacific appears in the observations such that xsP in South Pacific remains mostly above ~0.1 μM, whereas it is lower than 0.1 μM in the North Pacific. This suggests that Fe is preventing N_2 fixation in the South Pacific but not in the North Pacific, where atmospheric Fe deposition is much higher. The high xsP water that flows out of the ETSP denitrification zone into the Southern Ocean may remain high in xsP until it reaches a region with sufficient Fe (e.g., North Atlantic or North Indian Ocean), which could take several hundreds of years, and result in a significant decoupling of N_2 fixation from denitrification that occurs in the Fe-depleted Southern Hemisphere (see also *Falkowski* [1997]).

4. Conclusion

Model simulations that include Fe limitation of diazotrophy show a much better agreement with $\delta^{15}NO_3^-$ and xsP observations compared to a model that neglects this effect (Table 2, Figures 2, 3). Nitrate isotope observations show a decreasing northward trend across two transects in the Central and Western Pacific (Figure 3). Comparisons with model results reveal that these trends can be best explained by the input of isotopically light N by N_2 fixation, where higher rates of atmospheric Fe deposition exist. This highlights the potential of $\delta^{15}NO_3^-$ as a tool to infer the spatial pattern of N_2 fixation. If no N_2 fixation was occurring, the $\delta^{15}NO_3^-$

187 value would be expected to be very high ($\delta^{15}NO_3^- > 10‰$) due to the nearly complete utilization
188 of surface NO_3^- in the oligotrophic ocean [*Altabet and Francois*, 1994; *Somes et al.*, 2010],
189 which is a drastically different $\delta^{15}N$ signature than what would be expected if N_2 fixation was
190 significantly contributing to the local N pool ($\delta^{15}N_2 = 0‰$). Our results suggest that $\delta^{15}N$
191 observations, in combination with models, can be used to constrain N_2 fixation patterns in
192 present and past oceans.
193

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296

Figure Captions:

Figure 1. Top Panel: Annual rates of dust deposition [*Mahowald et al.,* 2005] and *FeL* parameter used to decrease the growth rate of diazotrophs. Bottom Panel: Vertically integrated N_2 fixation in FeLim and CTL.

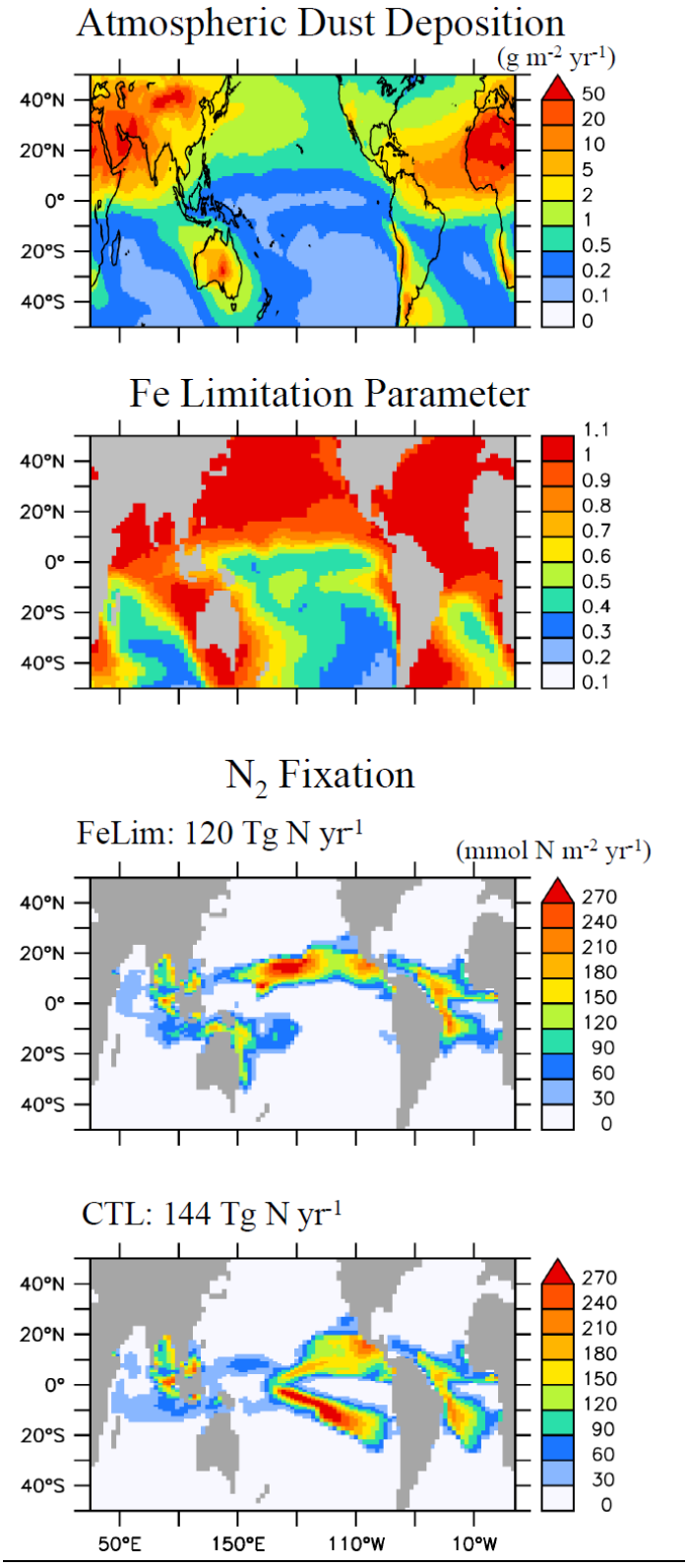
Figure 2. Comparison of FeLim and CTL with $\delta^{15}NO_3^-$ observations [*Somes et al.,* 2010] and World Ocean Atlas 2005: xsP = $PO_4^{3-} - NO_3^-/16$ and near-surface (0 – 100m) NO_3^- contours of 5.0 and 0.5 μM. Note that due to the too low N:P for diazotrophs in the model (N:P = 16:1) compared to observations (N:P = ~50:1) [*Letelier and Karl*, 1996; 1998], a slight overestimation of xsP is to be expected where N_2 fixation occurs.

Figure 3. Comparison of FeLim and CTL $\delta^{15}NO_3^-$ with observations in the (a) Central Equatorial Pacific (140°W) (100 – 250 m) [*Altabet,* 2001] (reanalysis), and (b) Western North Pacifc (100 – 250 m) (model transect connects through latitude/longitude of each data point): (A) ~6.75‰ at 0°N/S, 140°E [*Yoshikawa et al.*, 2006]; (B) ~6.0‰ at 6°N, 125°E [*Kienast et al.,* 2008]; (C) ~3.0‰ at 25°N, 123°E [*Liu et al.,* 1996].

	$\delta^{15}NO_3^-$			Excess P		
Model	***r***	***STD***	***RMS***	***r***	***STD***	***RMS***
CTL	0.668	1.76	1.33	0.520	1.30	1.27
FeLim	0.680	1.33	0.982	0.530	0.898	1.01

Table 1. Global measures of $\delta^{15}NO_3^-$ and xsP model performance: correlation coefficient (r), standard deviation (STD), and root mean squared (RMS) error. STD and RMS have been normalized by the standard deviation from the observations.

317 Figure 1.



318

Figure 2.

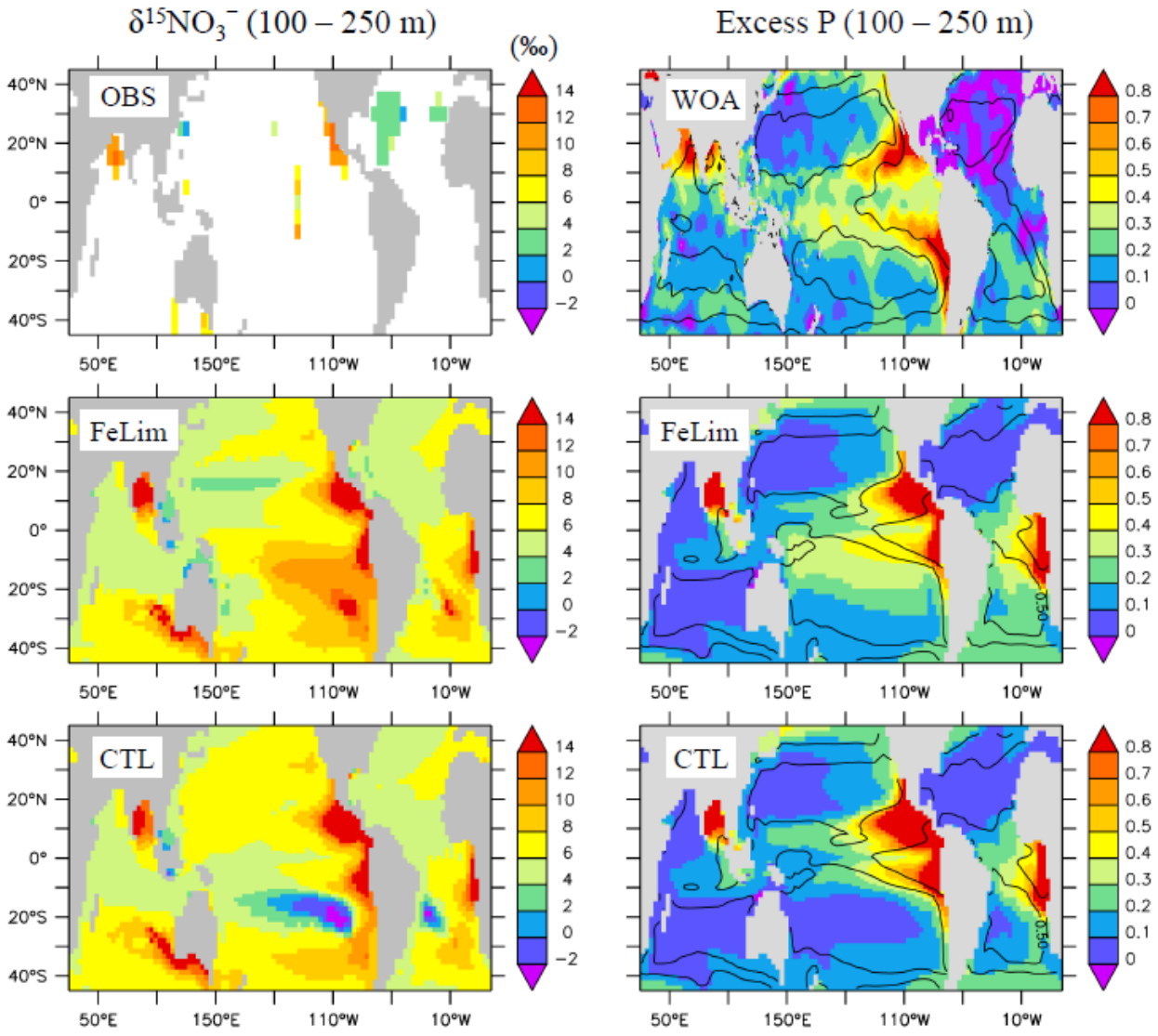
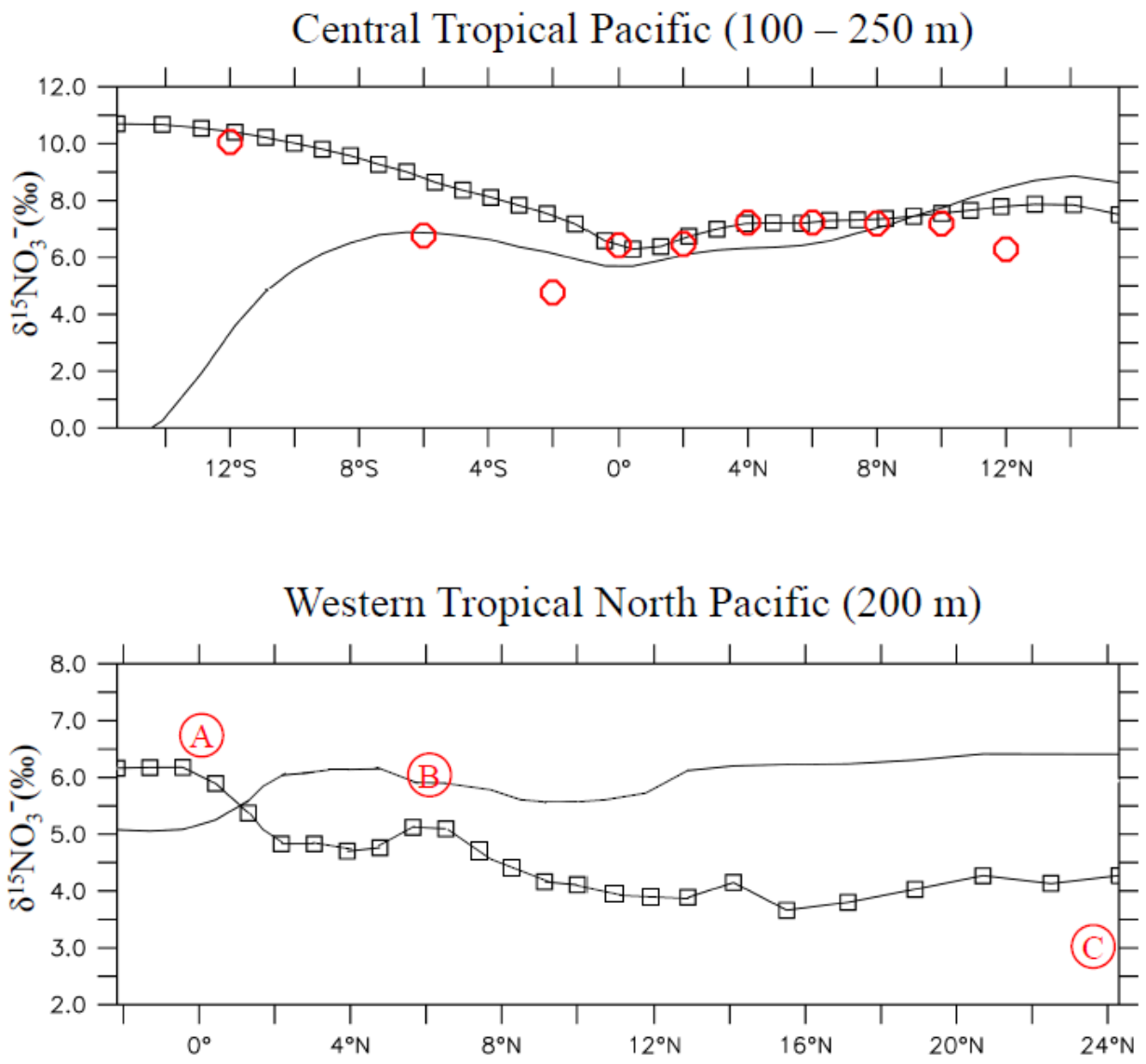

δ15NO3− (100 – 250 m)
(‰)
Excess P (100 – 250 m)
OBS
WOA
FeLim
FeLim
CTL
CTL
40°N
20°N
0°
20°S
40°S
50°E
150°E
110°W
10°W
14
12
10
8
6
4
2
0
−2
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

Figure 3.


Central Tropical Pacific (100 – 250 m)
$\delta^{15}NO_3^-$ (‰)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
12°S
8°S
4°S
0°
4°N
8°N
12°N
Western Tropical North Pacific (200 m)
$\delta^{15}NO_3^-$ (‰)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
A
B
C
0°
4°N
8°N
12°N
16°N
20°N
24°N