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N* variation within the Eastern Tropical North Pacific

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NONTECHNICAL SUMMARY

N* is a summary parameter used to describe areas of the ocean as either sources or sinks of fixed nitrogen, with positive values denoting nitrogen fixation (a source) and negative values signaling denitrification (a sink). Nitrogen is a major limiting nutrient of biological productivity, so this parameter is useful to differentiate productive regions from decaying regions in the global oceans. I used this parameter to trace water masses by suggesting that the N* signature is a result of the age and source location of different currents. I predict that currents with more productive source locations will have more negative N* values due to increased decomposition of fixed nitrogen caused by breakdown of organic matter by bacteria within the water column. I also predict that older water masses will have more negative N* because the organic matter within the water column would have had more time to be decomposed by these bacteria. By labeling different water masses with separate N* values then levels of mixing could also be identified as a middle number between these end member quantities. I answered these hypotheses using data collected on a cruise of the Eastern Tropical North Pacific (ETNP) in spring 2012 and used this data to provide a more detailed picture of fixed nitrogen breakdown within this region.

ABSTRACT

N* variation within the Eastern Tropical North Pacific (ETNP) was investigated to identify whether the zone of denitrification within this region had expanded since 1994 using data collected by the World Ocean Circulation Experiment (WOCE) program. Comparisons of April 1994 WOCE data and April 2012 data (collected on board the RV Thompson) along the same transect (northward on 110°W) showed that the core of the denitrification zone has intensified, with N* values becoming more negative from -12.5 µmol L-1 in 1994 to -17.5 µmol L-1 in 2012, and has increased vertically by roughly 150m. By following this -12.5 µmol L-1 isoline the lateral extent of this zone can be seen to have increased since 1994 to beyond the extent of the 2012 survey. The use of N* as a quasi-conservative tracer of water masses was also attempted by predicting that the N* signature is related to the age and source location productivity of said water mass. I predicted that more productive source regions resulting in more negative N* due to the presence of more organic matter, allowing more denitrification to occur. I also predicted that older water masses have more negative N* values because the organic matter present was exposed to denitrifying bacteria for a longer time period. I found that the relationship between a water mass and its N* value is more complex than I first thought and is dependent on many more variables than first thought.

It has been widely accepted that fixed nitrogen, in its various chemical species, is the major limiting nutrient in primary productivity within the contemporary global ocean (Tyrrell 1999; Falowski 1997; Codispoti 1989). Elemental nitrogen is not globally scarce, the atmosphere contains 70.08% N2 (Williams 2010), however very few organisms can utilize this chemically inert form of nitrogen due to the strong triple bond within the N2 molecule. Diazotrophs are nitrogen fixing cyanobacteria that can break this triple bond using the enzyme nitrogenase thereby increasing the biological potential of this element (Capone et al 1997). The reverse reaction denitrification is undertaken by bacteria and removes fixed nitrogen (specifically organic nitrogen and nitrate) from the oceans by turning it back into N2 gas. Nitrogen fixation and denitrification are the two major sources and sinks of bioavailable nitrogen with smaller sources being from riverine input and atmospheric deposition (Deutsch 2001; Arrigo 2005; Gruber 2008)

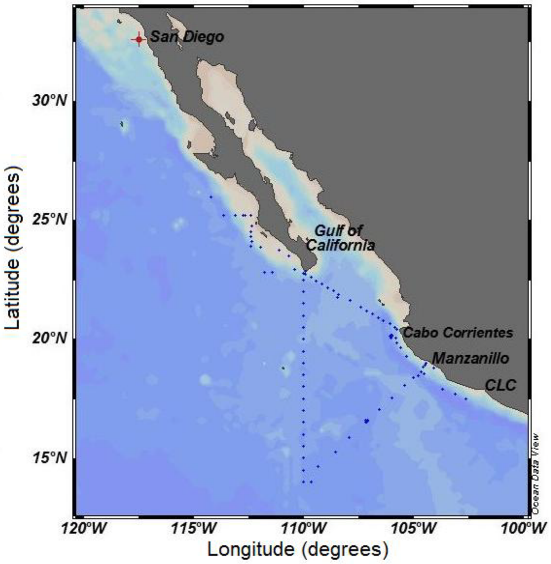

Figure 1. Map showing the sampling area of the ETNP; dots correspond to water sampling stations and major land marks are labeled (note CLC refers to Ciudad Lázaro Cárdenas)

Dinitrogen fixation is photosynthetically mediated so can only occur in the euphotic zone (Capone et al 1997, Gruber 2008), which means that as organic material sinks below this light layer no more N2 can be fixed. Instead the organic matter is affected by nitrification, denitrification and annamox (ammonium oxidation); nitrification produces bioavailable nitrogen species (nitrate, nitrite and ammonium) but requires oxic waters. Denitrification and annamox occur in suboxic to anoxic waters as these reactions are less energetically favourable than aerobic respiration (Codispoti 1989). The Eastern Tropical North Pacific (ETNP) is renowned for having one of the world's largest oxygen minimum zones (OMZ) (Paulmier and Ruiz-Pino 2009) and the associated denitrification with these suboxic to anoxic waters is also very large.

Once a water mass leaves the surface euphotic zone or organic matter sinks into a sub-euphotic zone water mass the organic material will begin to be aerobically remineralized. Once suboxia is reached (transition from oxygen to nitrate respiration) at oxygen concentrations of roughly 0.7 µmol L-1 (Yakusev and Neretin 1997) the major impact on that water masses bioavailable nitrogen inventory will be denitrification (a term that in this paper includes annamox) and this assumption will allow water masses to be labeled with a quasi-conservative N* tracer.

N* is a mathematically derived parameter created by Gruber and Sarmiento (1997) and subsequently modified by Deutsch et al (2001) that can be used to describe the productivity of a region of water by quantifying the deviation from Redfield ratios (1934, 1963) of nitrogen to phosphorous (16:1).

$$N^* = DIN - 16P + 2.90\ \mu mol\ L^{-1}$$

DIN is the total dissolved inorganic nitrogen concentration (nitrate, nitrite and ammonium) and P corresponds to phosphate concentrations. The 2.90 µmol L-1 constant is required so that if Redfield ratios of 16DIN: 1PO4 were observed the resultant N* would be zero; this is necessary due to the residual concentration of phosphate that is always present once all fixed nitrogen has been utilized.

This equation is useful to describe regions of the ocean as either net sources or sinks of fixed nitrogen. This is because a positive deviation from Redfield ratios (1934, 1963) suggests water has a DIN: P ratio greater than 16 (excess fixed nitrogen) which can only occur due to nitrogen fixation, which would result in the above equation producing a positive N*. Conversely a negative deviation from 16DIN: P suggests there is reduced fixed nitrogen compared with 'expected' Redfield values and so bioavailable nitrogen is being removed from the water column and this would mathematically produce a negative N*. The use of this equation to differentiate between sources (+N*) and sinks (-N*) of fixed nitrogen also explains why I have included annamox reactions within the denitrification term; mathematically annamox cannot be distinguished from denitrification.

Three main currents circulate within the ETNP; the California Current (CC), the Mexican Coastal Current (MCC) and the Gulf of California outflow (GC outflow) (Godinez et al 2010). These currents can be identified using their distinct physical characteristics; the CC has relatively low temperatures and salinities (Fiedler and Talley 2006), the Mexican Coastal Current travels within 100km of the coast and flows poleward with warm and slightly saline physical properties (Lavin et al 2006) and the GC outflow has high temperatures and salinities (>35) (Roden 1971).

OMZs are predicted to increase with future climate change and this will see a corresponding increase in the denitrification zones associated with these low oxygen areas (Paulmier and Ruiz-Pino 2009). Investigating the extent of the denitrification zone could highlight whether this zone has already increased spatially, which may provide insight into the rate of climate change or amount of nitrogen fertilizer pollution in this region – my first hypothesis states that the zone of denitrification, associated with the OMZ, will have increased spatially compared to data collected in 1994 during the World Ocean Circulation Experiment (WOCE) program.

My second hypothesis relates N* to the age of a water mass; I predict that the older a water mass then the more negative (more denitrifying) the N* signal due to the decrease in oxygen concentration and increase in organic detrital material that occur as a water parcel ages. Comparisons between the old upwelled water along the coast of Baja California to relatively young water masses circulating from the north will give qualitative estimates of the relation of N* to age. Water mass age tracers were unavailable for this cruise so the ages will be qualitatively estimated using previously published physical data from this region.

The distinct physical characteristics and surface source region characteristics of the three major water masses circulating through the ETNP will test my third hypothesis that N* of a water mass is related to the source characteristics of that water mass.

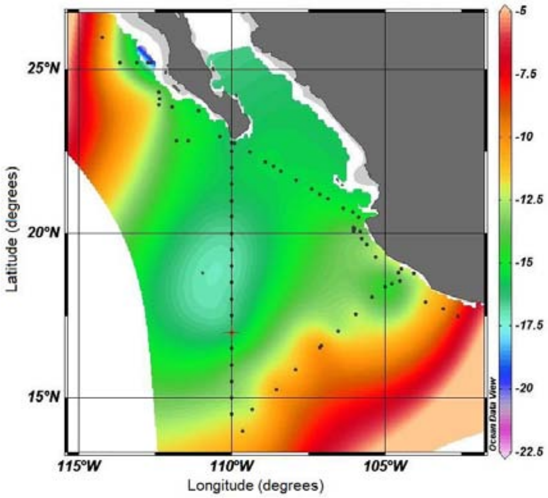

Figure 2; N, in µmol L-1, at 200m depth. Dots correspond to data collection sites, with white regions denoting areas too far from data to be interpolated.*

METHODS

Water samples were collected throughout the ETNP and analyzed on board the RV Thompson in March and April 2012. I collected and analyzed water samples taken in the first two legs of the cruise; the first being from San Diego, California, to Manzanillo, Mexico, and the second between Ciudad Lázaro Cárdenas and Cabo Corrientes along the coast of Mexico (Figure 1). The third leg of the cruise travelled offshore from Manzanillo into the main ETNP basin then transited northward along 110°W allowing data collected here to be directly comparable with 1994 WOCE data. Associates from the University of Washington collected and analyzed the water samples from this third leg and kindly shared their results.

Water samples were collected in Niskin bottles within the top 2000m (unless bottom depth was shallower), with higher resolution within the top and bottom oxyclines of the oxygen minimum zone so as to fully identify the region of denitrification. Oxygen concentrations were measured using an SBE 43 oxygen electrode and temperature, salinity and pressure were recorded using a Sea-Bird Electronics 911plus CTD with both of these instruments attached to the Niskin

Rosette. Nitrate, nitrite, ammonium, and phosphate concentrations (measured in µmol L-1) were determined from these water samples using a Technicon Autoanalyser II following the procedures outlined in the UNESCO JGOFS guide (1994). The method detection limit of these nutrients were; 0.08 µmol L-1 NO3, 0.01 µmol L-1 NO2, 0.07 µmol L-1 NH3 and 0.03 µmol L-1 PO4. Ocean Data View was used to plot and interpolate results.

RESULTS

Expansion of the denitrification zone;

Figure 2 shows that the zone of denitrification has a central core with a minimum N* value of roughly -16.5 µmol L-1 along the 200m isosurface and that N* becomes less negative (decreasing denitrification) radiating from this core reaching roughly -15 µmol L-1 off the coast of Cabo St Lucas to the north, and with the transect from 14°N 110°W to the coast of Manzanillo tracing the

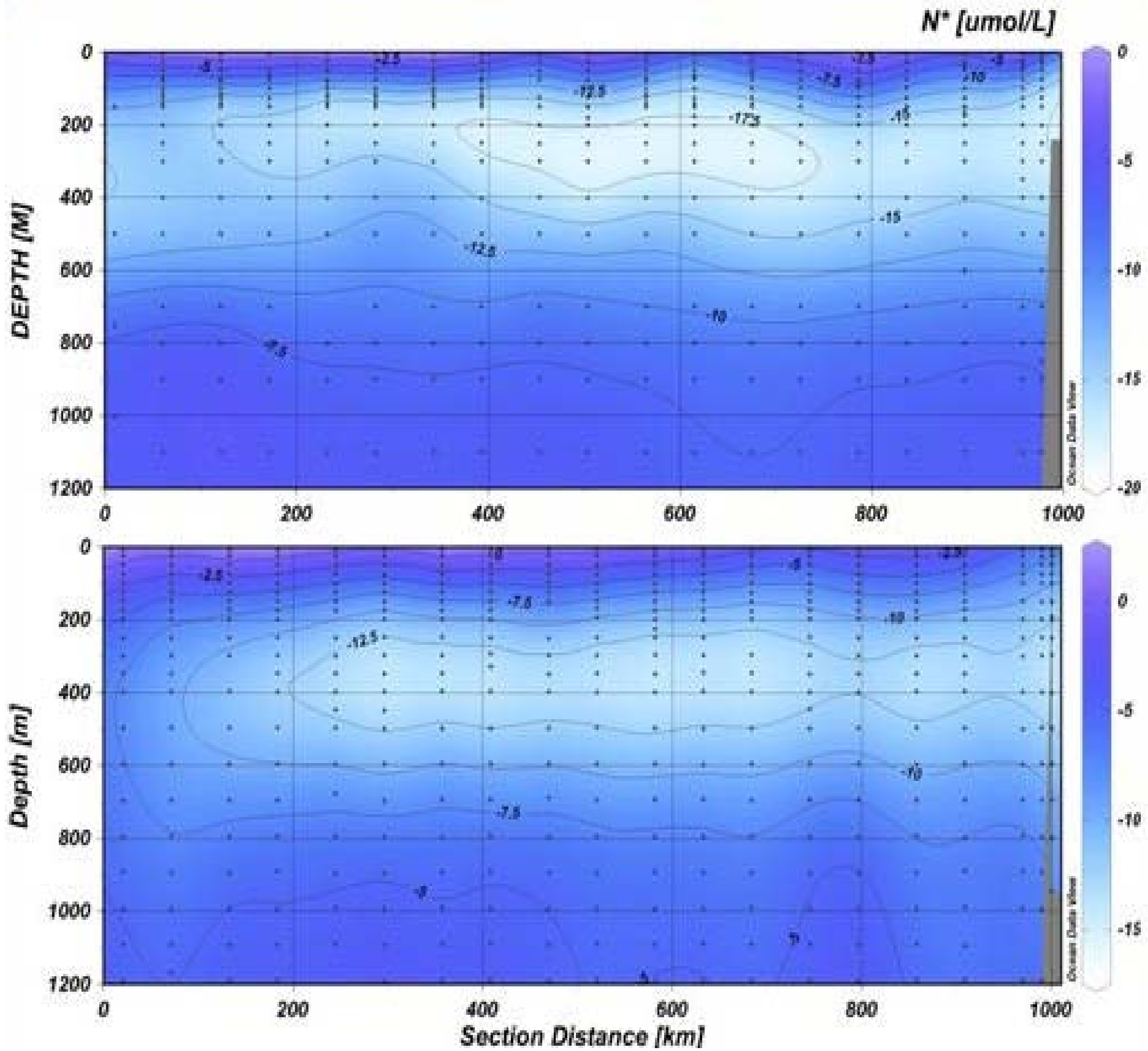

Figure 3; transect travelling northward along 110°W beginning at 14°N and ending at the coast of Cabo St Lucas (1000m on the section distance). Top graph shows data collected in March and April 2012 on board the RV Thompson and the bottom graph shows data collected by the WOCE program in April 1994. Small dots represent water samples and solid lines represent isovalues of N at intervals of 2.5 µmol L-1. (Appendix 1 shows a map of the transect)*

-12 µmol L-1 N* concentration isoline. Unfortunately the Ocean Data View (ODV) interpolation of the data creates a misleading image whereby the N* values rapidly become less negative outside of the study area, reaching 0 µmol L-1 roughly 100km from sampling locations; this is simply an artifact and so these trends cannot be verified. However this graph does show two excursions of denitrified water (N* between -15 and -13 µmol L-1) extending along the coast of Baja California to the north and along the coast of mainland Mexico to the south. These excursions are based on real data and are not simply due to interpolation error as can be seen from the number of water samples collected along these coasts (grey dots in figure 2). A high level of denitrification can also be identified along the Baja Coast (at roughly 25°N 113°W) with an N* value between -20 and -22 µmol L-1.

The transect northward along 110°W (figure 3) gives a more representative picture of the vertical and lateral extent of the denitrification zone between April 1994 (bottom) and April 2012 (top). In 1994 the maximum negative N*was roughly -12.5 µmol L-1 and was situated at roughly 400m deep extending roughly 800km southward from the coast of Cabo St Lucas. In 2012 the maximum negative N* had increased to -17.5 µmol L-1 and this more intense core of denitrification was shallower, at around 300m deep, and was approximately 400km wide. The N* region with values more negative than -12.5 µmol L-1 has increased spatially since 1994; the vertical extent has almost double from approximately 250m in 1994 (between 250 and 500m depth) to 400m in 2012 (between 150 and 550m). Laterally this zone has extended from ending 800km offshore Cabo St Lucas to beyond the extent of the 2012 survey.

Identifying water masses and labeling with N;*

The temperature salinity plot (figure 4) allowed different water masses to be identified by their physical properties and then labeled with an N* signature. Six water masses were identified from this plot; the Antarctic Intermediate Waters (AAIW) were very cold waters (below 5°C) found at depths greater than 1000m and had surprisingly non-denitrified waters with N* values between -5.6 and -2.9 µmol L-1. I created the term ETNP surface waters to describe the warm, low salinity waters that were found at the surface in the middle of the survey area; this water had N* values ranging from -2.7 to -0.3 µmol L-1. GC waters were identified by their high temperatures (19 - 15°C) and salinities (>34.7) and had N* values of roughly -8.0 to -6.8 µmol L-1. The CC was identified by relatively low temperatures (10 - 19°C) and salinities (33.5 - 34) and had the largest range in N* values from -1.5 to -10.1 µmol L-1. The highest negative N* values were found within what appeared to be a single water mass on the temperature – salinity plot but that I differentiated into two different water masses; the water mass with N* values more negative than -15 µmol L-1 (to a maximum negative value of -17.6 µmol L-1) were determined to be 13°C as defined by Fiedler and Talley (2006) whilst the water mass with N* values between -13.9 and -9.2 µmol L-1 was determined to be MCC.

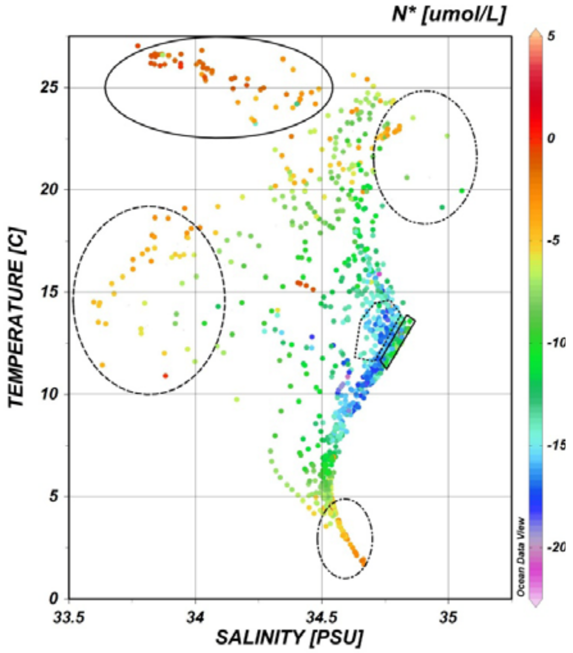

Figure 4. temperature salinity plot identifying different water masses by their temperature and salinity properties. Solid ellipse denotes ETNP surface water, dashed ellipse denotes coast of Baja California surface waters (possibly the California Current), dashed-dot ellipse denotes Antarctic intermediate water (AAIW), dashed-dot-dot ellipse denotes Gulf of California water (GC), dotted polygon denotes 13°C water and the solid polygon denotes Mexican coastal water (MCC).

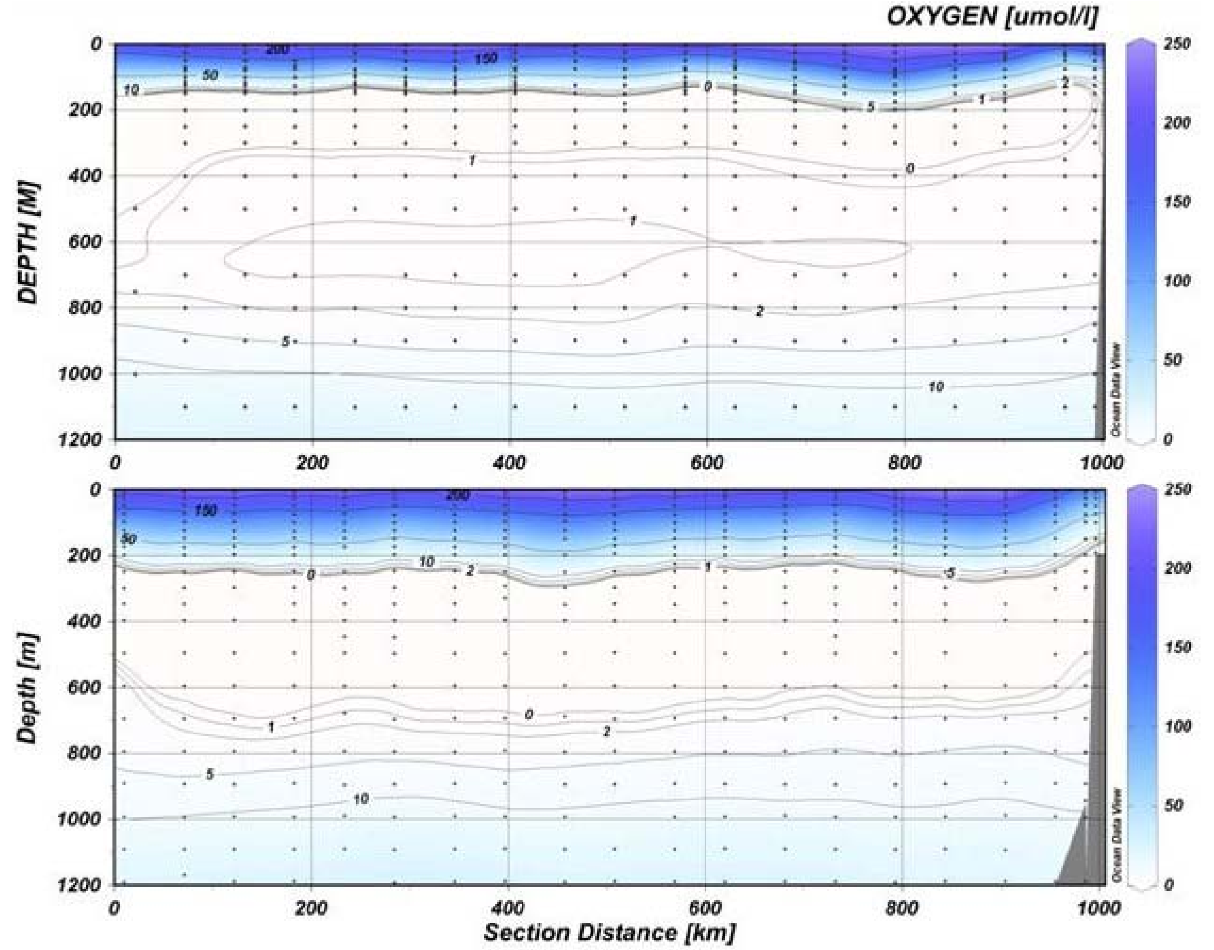

Figure . Oxygen concentrations in µmol L-1 along 110°W up to the coast of Cabo St Lucas. Top graph shows data collected in April 2012 and the bottom graph shows data collected by WOCE in April 1994. Small dots represent water samples and solid lines represent equal oxygen concentrations with the concentration written on each line. (Appendix 1 shows a map of the transect).

Expansion of the denitrification zone;

Figure 3 suggests the denitrification region within the ETNP has not only increased but has also intensified. This increase in the size and intensity of the denitrification zone can be explained by the increase in the size of the oxygen minimum zone where concentrations are below 1 µmol L-1. This central low value could be caused by convergence of water masses effectively trapping organic material within the centre of this ocean basin.

The excursion of highly negative N* along the coast of Baja California (figure 3) suggest denitrifying water is being carried north within a current. This current carrying denitrifying water

CONCLUSIONS

Expansion of the denitrification zone;

The denitrification zone appears to have increased and intensified which could provide evidence for the impact of global warming on this region of the ocean. To fully see the parameters of this newer, larger denitrification zone expansion of the study area should be undertaken to identify any trends and whether the ODV interpolation of the data into concentric rings expanding from a central maximum denitrification zone is accurate or whether this denitrification zone is more complex than initially considered.

The use of N* as a tracer of water masses could be useful as in the situation where 13° water was differentiated from MCC water however the relationship between N* age and source location productivity is not as linearly simple as I first estimated and is in fact a result of both the age and source location productivity. Other factors must be taken into account including the depth of the water mass in the water column; the further organic matter has to sink before being entrained in a water mass will have a large effect on the N* signature of the water. Also completely countering my hypothesis that more productive source regions would create more negative N*, Arrigo (2005) has found that the species composition of the water could have a large effect on the initial DIN: P ratio of the water column with oligotrophic regions having higher N: P ratios (>30 μmol L-1) than 'bloom' type regions where the N: P ratio (<10 μmol L-1).

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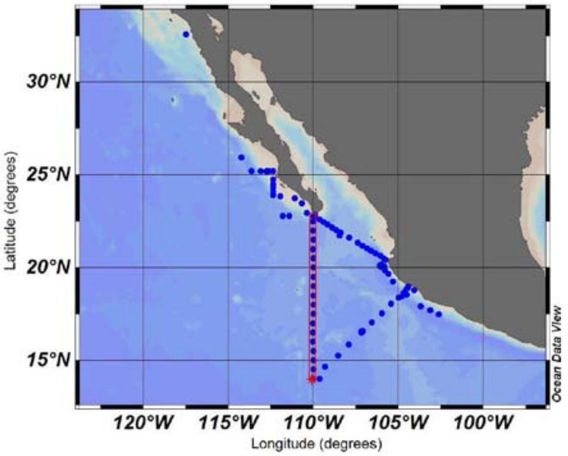

Appendix 1; the red box highlights the transect along 110°W where WOCE and my data were collected; blue dots within the box denote water sample stations from the 2012 cruise. Surrounding blue dots correspond to other water sample stations on the 2012 cruise. The transect began at 14°N 110°W and travelled 1000km northward to the coast of Cabo St Lucas.