NOAA Office of Ocean Exploration and Research

FINAL Report (due: 11/29/2019)

I. Overview

1. Grant Number: NA16OAR0110196
2. Amount of funding from OER:
3. Project Title: "Profiling Sensor to Map N_2 Gas Production in OMZs"
4. Area of Operation:
5. Principle Investigator:

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6. Participating Institutions and personnel

   Craig McNeil (PI, APL), Eric D'Asaro (co-PI, APL), Mark Altabet (co-PI, University of Massachusetts Dartmouth), Annie Bourbonnais (Assistant Professor, University of South Carolina), Trina Litchendorf (Field Engineer and Chemical Oceanographer, APL). Dr. Andrew Reed, who participated in the NOAA Okeanos cruise, is now graduated and employed by Woods-Hole Oceanographic Institute (WHOI, MA) as a Research Associate III in the Applied Ocean Physics and Engineering department (https://www.whoi.edu/profile/areed/).
7. Award Period: 09/01/2016 - 08/31/2019
8. Period Covered by this Report: **09/01/2016 - 08/31/2019**

II. Evaluation:

1. **Work Accomplishments:**
   - **1a.** As recommended in our last report, we have performed a comparison of the nutrient and gas tension based methods with an error analysis and found that we can explain the offsets between the two methods based on uncertainty in the absolute argon saturation levels.
   - **1b.** The data analysis and interpretation presented below is the basis of an instrumentation paper which we can now assemble.

2. **Expenditures:**
   - **2.a.** We are spent out on this grant and are beginning the close out process.

3. <u>Results</u>:

3a. A primary technical objective of this work was to develop a fast response gas tension device (GTD) to measure gas tension in seawater on a profile CTD system. We achieved this goal early on by a combination of advances: 1) we replaced the large dead-volume pressure sensor used in prior GTDs with a low dead-volume micro electro-mechanical system (MEMS) barometric pressure sensor, 2) we used a customized fast-response Teflon AF gas permeable membrane, and 3) we developed and implemented a plenum that achieves an evenly spreading flow of seawater over the entire surface of the membrane to maximize shear at the membrane-seawater surface to enhance gas transfer. The new GTD (see Fig. 1, upper left) has a response time of less than 2 minutes and an operating depth range of 0-1000 m. This is a great addition to the Chemical Oceanographer's toolbox and a significant deliverable of this project. The new GTD is now commercially available through Pro-Oceanus Systems, Inc.

3b. Complementing this new GTD sensor, a primary technical objective of this work was to refine, test, and validate the gas-tension-based method to derive excess- and biogenic-nitrogen against more labor intensive existing methods (see Fig. 1, lower right) which include the nutrient-deficit and mass-spectrometric based approaches. Prior to the technical development described in 3a, no gas tension profile data across an open ocean ODZs was available to perform these methods inter-comparisons. Use of the new profiling GTD on the NOAA Okeanos cruise between Hawaii and Panama allowed us to collect the first data set to perform a comparison of methods. Although we had difficulty with storage of the samples use for mass-spectrometric analysis, which was likely due to slow leaks in the storage bottles, we were able to successfully collect and analyze independent nutrient-based estimates of biogenic N_2 for comparisons. The rest of this report describes in more detail these measurements and inter-comparisons and the interpretation of the data and concludes with a summary of our findings.

3c. Let us first review how we measured biogenic N_2 across the ETNP for this project. We developed a new gas tension device and used it, for the first time, to measure vertical profiles of gas tension, along with vertical profiles of dissolved O_2, temperature (T) and salinity (S) across the ETNP on the NOAA Okeanos Explorer cruise. Dissolved N_2 was calculated from:

$$pN_2 = P_T - pO_2 - pH_2O - pTrace \qquad \text{Eqn. (1)}$$

using Henry's Law: N_2 (umol/kg) = $S_H(T, S)$ x pN_2. Solubility coefficients (S_H) and water vapor pressure (pH_2O) are known functions of water temperature (T) and salinity (S). Partial pressures of trace gases (including argon) are relatively small and can be accounted for in the calculations with little error (*Reed et al., 2018*). For the anoxic ODZ core, pO_2 =0. Small changes in non-zero O_2 is accounted for with little error in determined N_2 using the dissolved oxygen sensor on the ship's CTD. In the ODZ core waters, we get direct measurements of 'excess' N_2 (ΔN_2^{excess}) defined as the difference between the measured N_2 concentration ($N_2^{measured}$) and the calculated N_2 solubility, N_2 concentration ($N_2^{\text{solubility}}$) for seawater in equilibrium with the atmosphere at in situ temperature and salinity and unaltered by denitrification, thus:

$$\Delta N_2^{excess} = N_2^{measured} - N_2^{solubility}. \quad \text{Eqn. (2)}$$

Biogenic N_2 is then calculated as:

$$\Delta N_2^{bio} = \Delta N_2^{excess} - \Delta N_2^{physical\ background} \quad \text{Eqn. (3)}$$

where $\Delta N_2^{\text{physical background}}$ is an estimate of the portion of $\Delta N_2^{\text{excess}}$ produced by physical processes. There are different assumptions that can be used to determine $\Delta N_2^{\text{physical background}}$ in the source waters of the ODZ. The simplest is to assume $\Delta N_2^{\text{physical background}} = 0$, such that when the source waters were formed and subducted into the ocean they were initially saturated with respect to the atmosphere. We know that this assumption likely is poor because 1) air pressure at water mass formation cannot always be assumed to be one atmosphere due to the passage of weather systems, and 2) bubble injection processes during high winds produces supersaturations for weakly solubility gases such as nitrogen. A better approach is to use argon, an inert gas, as a proxy measurement for the saturation anomalies of weakly soluble gases such as nitrogen at water mass formation. Since argon can only be measured by precise mass-spectrometric techniques (e.g., isotope dilution), there are few measurements of argon concentration for the ETNP. However, one such study does exist for the ETNP region (*Chang et al., 2012*) and we use their regional measurements of argon versus potential density to estimate the $\Delta N_2^{physical\ background}$ by assuming that the N_2 and Ar saturation anomalies at formation were the same. We must assume no latitudinal or water-mass specific variations in $Ar^{measured}$ since the data set used in the study did not have enough spatial sampling to address this uncertainty. Thus, we used:

$$\Delta N_2^{physical\ background} + N_2^{solubility} = Ar^{measured} / Ar^{solubility} \times N_2^{solubility} \quad \text{Eqn. (4)}$$

Combining Equations (2), (3) and (4) we get:

$$\Delta N_2^{bio} = N_2^{measured} - Ar^{measured} / Ar^{solubility} \times N_2^{solubility} \qquad \text{Eqn. (5)}$$

Combining Equations (1) and (5) we get:

$$\boldsymbol{\Delta N_2^{bio} = (P_T - pO_2 - pH_2O - pTrace) \times S\, N_2^{(P,T,S)} - Ar^{measured} / Ar^{solubility} \times N_2^{solubility}} \qquad \textbf{Eqn. (6)}$$

where $SN_2^{(P,T,S)}$ in the in situ Henry's law parameter. We use the $\Delta N^{deficit}$ method as an independent estimate of biogenically produced N_2, using:

$$\Delta N^{deficit} = 16\times[PO_4^{3-}] - ([NO_3^-] + [NO_2^-] + [NH_4^+]) \qquad \text{Eqn. (7)}$$

where the equivalent nutrient based biogenic N_2 estimate is:

$$\Delta N_2^{bio} = \Delta N^{deficit}/2 \qquad \text{Eqn. (8)}$$

Combining Equations (6) and (7) we get:

$$\boldsymbol{\Delta N_2^{bio} = (16\times[PO_4^{3-}] - ([NO_3^-] + [NO_2^-] + [NH_4^+]))/2} \qquad \textbf{Eqn. (9)}$$

In summary, we use Equation (6) to determine a direct estimate of biogenically produced N_2 from the new sensor and compare to an independent estimate derived from nutrient data using Equation (9).

References:

- Chang, B. X., Devol, A. H., & Emerson, S. R. (2010). Denitrification and the nitrogen gas excess in the eastern tropical South Pacific oxygen deficient zone. Deep Sea Research Part I: Oceanographic Research Papers, 57(9), 1092-1101.

- Reed, A., McNeil, C., D'Asaro, E., Altabet, M., Bourbonnais, A., & Johnson, B. (2018). A gas tension device for the mesopelagic zone. Deep Sea Research Part I: Oceanographic Research Papers, 139, 68-78.

3d. We use the World Ocean Atlas 2013 (WOA13, *Garcia et al., 2014*) for historical climatology with the caveats that the climatology does not have nitrite nor ammonia. Since open ocean ammonia concentrations in ODZ regions are typically zero, we set $[NH_4^+] = 0$ in Eqn. (9). For the WOA13, the reported values for nitrate concentration are actually reflective of nitrate plus nitrite. The regional climatological nutrient and $\Delta N^{deficit}$ maps are shown in **Figure 2** on the isopycnal 26.5 (kg/m^3) which is located at approximately 150 m depth and is the density range where the largest $\Delta N^{deficit}$ is expected due to active denitrification. Also highlighted on Figure

1 are two NOAA Okeanos Explorer Explorer CTD stations (Stations *F* and *H*) which are representative of the ODZ core waters.

References:
-Garcia, H. E., R. A. Locarnini, T. P. Boyer, J. I. Antonov, O.K. Baranova, M.M. Zweng, J.R. Reagan, D.R. Johnson, 2014. World Ocean Atlas 2013, Volume 4: Dissolved Inorganic Nutrients (phosphate, nitrate, silicate). S. Levitus, Ed., A. Mishonov Technical Ed.; NOAA Atlas NESDIS 76, 25 pp.

3e. Next we use the WOA13 climatology to help us understand where source waters that feed the ODZ core region come from and how these waters are biologically processed as they move into and through the ODZ core region. Shown in **Figure 3b** are plots of $\Delta N^{deficit}$ versus salinity taken from the WOA13 for a region 'upstream' of the ODZ core. These saltier and more oxygenated waters are considered 'source' waters to the ODZ core region and transported into the core region by the North Equatorial Current (see Fig. 3a). As these source waters move westward on the 26.5 isopycnal, the salinity decreases likely due to dilution by mixing and $\Delta N^{deficit}$ increases likely due to denitrification as the oxygen is respired and the waters become functionally anoxic by the time they reach the central ODZ core.

3f. With this oceanographic context, we proceed to inspect the NOAA Okeanos Explorer Explorer CTD station data and perform direct comparisons to climatology at select stations in the ODZ core. **Figure 4** shows these comparisons for $\Delta N^{deficit}$ on a TS plot which allows us to interpret the data based on mixing arguments. A straight line on a TS plot indicates dilution between two end-member water masses. The main water mass at a temperature of approximately 13 ºC is one such end member and is known as the '13 degree thermostad' waters. These waters are just below the main thermocline and are diluted with the overlying near surface waters, representing a loss of biogenic N_2 from the ODZ core waters. Similarly, mixing and dilution with deeper more oxygenated deeper waters below the ODZ core also represent a loss of biogenic N_2 to the deeper ocean. The core waters have the highest biogenic N_2 and can be seen in this plot at potential temperature of $\theta \sim 10$ ºC and $S \sim 34.65$ psu. Biogenic N_2 may be higher in shallower waters that are more influenced by the export of organic matter (C_{org}) from the photic zone since C_{org} is a requirement for active denitrification.

We conclude that the nutrient data taken on the NOAA Okeanos Explorer cruise are consistent with climatology and, in the absence of mass-spectrometric measurements, provide a good independent comparison for GTD-derived estimates of biogenic N_2.

3g. We now compare the NOAA Okeanos Explorer nutrient-derived estimates of biogenic N_2 (derived using Eqn. 9) with the GTD-derived estimates using measured excess N_2 and previously published estimates of Ar versus density (derived using Eqn. 6). These comparisons are shown in **Figure 5**, on a 1:1 scale plot with the GTD-derived estimates linearly offset by -24 μmolN_2/kg. The plot indicates a very good correlation barring some latitudinal dependence which may be due to unaccounted latitudinal dependence in the argon concentrations. The reason for the very large offset is now investigated using an error analysis.

3h. Shown in **Figure 6** is a sensitivity analysis of the same calculations presented in Figure 5 based on varying two key parameters: 1) the concentration of nitrite, which was unmeasured on the Okeanos cruise but assumed based on climatology, 2) the concentration of argon ($Ar^{measured}$, see Eqn. 6), which likewise was unmeasured on the Okeanos cruise but measured previously by other colleagues at UW in the ETNP ODZ [courtesy of Bonnie Chang and Clara Fushman]. The uncertainty in nitrite concentrations introduces an uncertainty in biogenic nitrogen of $< \pm 0.5$ μmolN_2/kg, which is relatively small compared to the very large offset of 24 μmolN_2/kg between the two methods. To account for this offset within experimental uncertainty, we increase the UW argon concentrations by 5.5%.

3i. To summarize, we report an inter-comparison between the gas-tension method and the nutrient-deficit method that identifies the major source of uncertainty as the dissolved argon concentration. Improved surveys of dissolved argon variability will enable improved estimates of biogenic N_2 from the measured excess-N_2 determined by the gas tension method. We conclude that improved knowledge of the spatial and temporal variability of argon within ODZs will provide improved accuracy in biogenic N_2 estimates derived from excess N_2 using the gas tension method. Since argon is inert, we expect that argon variability likely occurs over large-spatial and long-temporal scales compared to excess N_2 variability associated with denitrification processes. We continue to advocate for excess N_2 surveys in ODZs using the new GTD sensor, which are immune to uncertainty in argon, to identify baseline inventories. We also recommend concurrent sampling for argon concentrations where possible to improve biogenic N_2 estimates from these gas tension-derived excess N_2 surveys. Longer term plans to detect ODZ excess N_2 and biogenic N_2 changes associated with global warming related impacts that utilize the new GTD technology should proceed.

4. **Publications and presentations**

(1) PhD thesis by Andrew Reed (who successfully defended on 03/09/2018) titled: 'A Gas Tension Device & Method for Denitrification Studies in Oxygen Minimum Zones', School of Oceanography at University of Washington (advisors McNeil and D'Asaro).

(2) Reed, A., McNeil, C., D'Asaro, E., Altabet, M., Bourbonnais, A., & Johnson, B. (2018). A gas tension device for the mesopelagic zone. Deep Sea Research Part I: Oceanographic Research Papers, 139, 68-78.

(3) McNeil, C. L., D'Asaro, E. A., Reed, A., Altabet, M. A., Bourbonnais, A., & Beaverson, C. (2018). Innovative nitrogen sensor maps the North Pacific oxygen minimum zone, *Oceanography– Supplement- New Frontiers in Ocean Exploration*, 31(91):96.

(4) Mark Altabet, Autonomous observation of oxygen deficient zone (ODZ) biogeochemistry, presented at Ocean Deoxygenation Conference, 3-7 September, 2018 in Kiel University, Germany (conference website: https://conference.sfb754.de/event/1/).

5. **Review of original proposal goals and objectives**

Notation is original goals/objectives (italic) and responses (bold):

"GOALS AND OBJECTIVES Driven by the need to detect any increase in denitrification due to ocean deoxygenation over the next decade, our overarching goals are:

1) Enable rapid and cost-effective measurement of N_2 distributions in OMZs within 1 year. **[complete]**

2) Collect baseline measurements of N_2 in the ocean's OMZs within 3 years. **[started]**

3) Start resolving variability in baseline measurements of N_2 expected on decadal time scales. **[needs commitment and a plan going forward]**

The primary objectives of the proposed work are:

1) Develop a low production-cost profiling GTD to measure N_2 in OMZs to better than ± 0.3% with a response time of 10's of seconds using a low volume pressure sensor and a pumped Teflon-AF 2400 membrane interface. The new sensor will be insensitive to hydrostatic pressure changes, operate to depths of at least 1000 m, and be compatible with rapid-profiling oceanographic platforms (e.g., gliders, AUVs, wire profilers) where power constraints are not severe and both pre- and post-deployment calibrations are possible. **[95% done; Our field tests of the new GTD were limited to 600m, but it has been mechanically**

leak-proof tested in the lab to 1000 m and ProOceanus have performed basic tests of the membrane interface to 4000m without issue.]

2) *Validate the new sensor using mass-spectrometric determination of N_2 and an existing slower-response GTD in the local waters of Puget Sound and in the Eastern Tropical Pacific.* **[incomplete, we had problem with the storage of samples for IRMS analysis]**
3) *Commission the new sensor on a Pacific Sector NOAA Ship (e.g., Reuben Lasker), and install a second system on an Atlantic Sector ship (e.g., Ronald H. Brown), for use in baseline monitoring of OMZs* [**50% done: *Ruben Lasker* -> *Okeanos Explorer* but using *Robertson*'s CTD, with no funds left for *Brown***].
4) *Start producing global maps of oceanic N_2."* [**started, we are also now recently funded by NSF to pursue mapping O_2 and N_2 in the ETNP by floats using grant "Collaborative Research: Multiyear autonomous measurement of N-loss in the ETNP ODZ", NSF OCE awards 1851210 (PI Eric D'Asaro; Co-PI Craig McNeil) and 1851361 (PI Mark Altabet); 03/01/2019 – 02/28/2023.**

Prepared By:

____ 11/29/2019

Signature of Principal Investigator Date

FIGURES

Figure 1. A photograph of three newly developed fast response GTDs (upper right) developed for this project and a photograph of the new sensor being used on the ship's CTD (lower right).

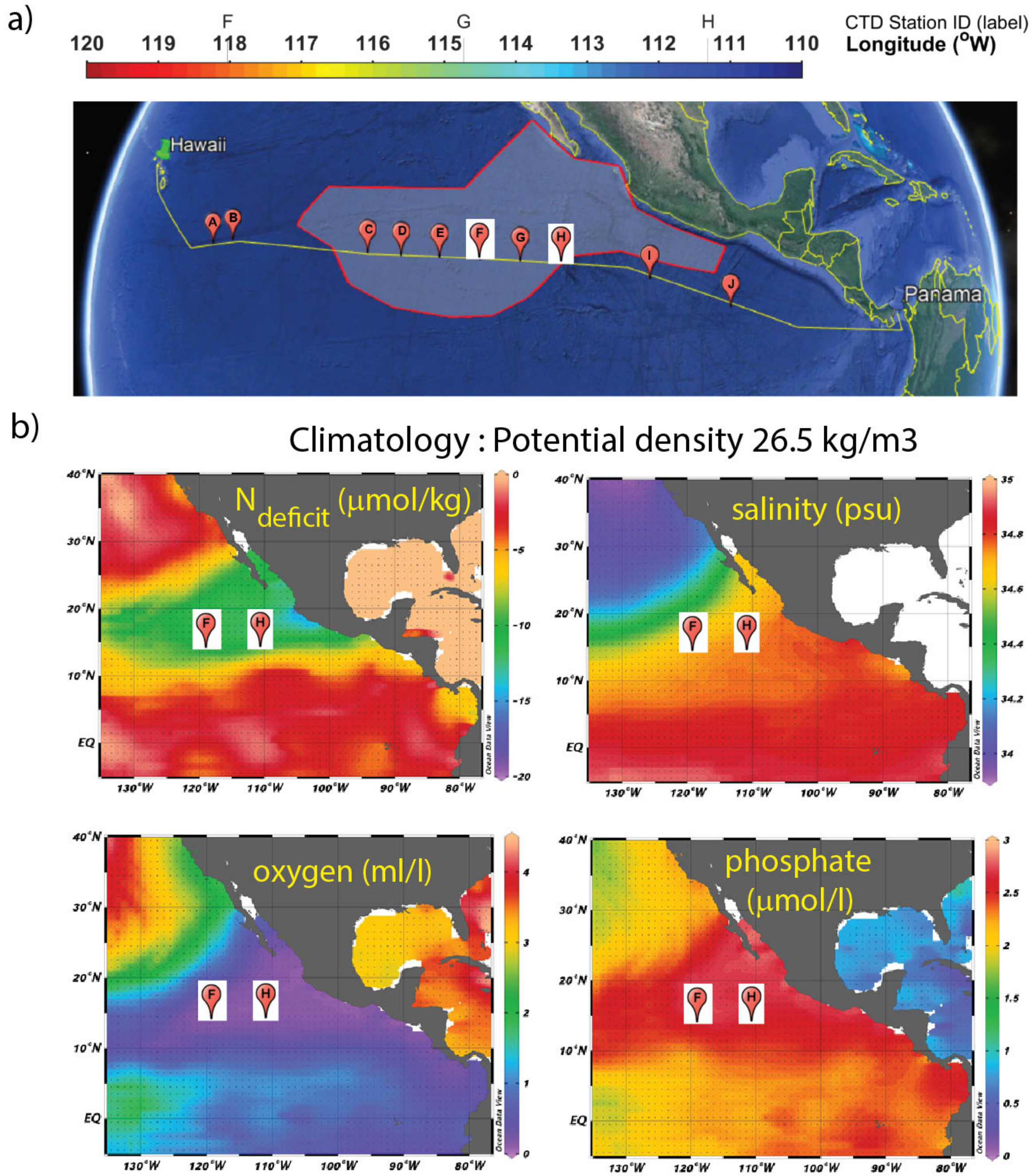

Figure 2. Overview of the NOAA Okeanos Explorer shipboard data in context of climatology, showing: a) Location of CTD stations (red markers) made during the cruise with highlighted Stations F and H overlaid on a Google Earth map of the Eastern Pacific marked (shading) to show the anoxic core, and a legend to relate CTD station ID with longitude; and b) Climatological maps on potential density surface (isopycnal) of 26.4 kg/m^3 of nutrient deficit estimate of $\Delta N^{deficit}$, salinity, dissolved oxygen and phosphate.

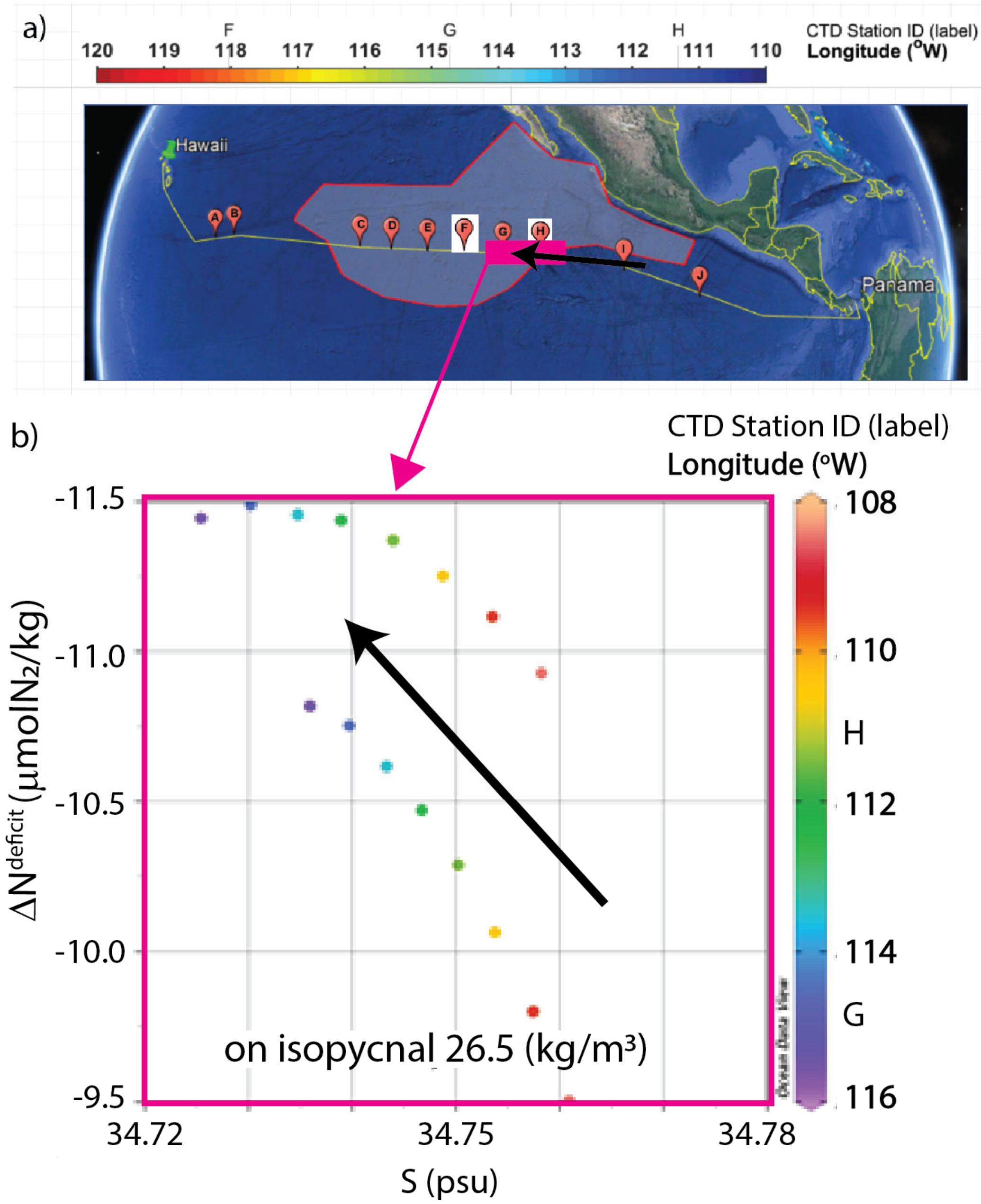

Figure 3. Physical context for the ODZ core region, showing: a) Map with highlighted NOAA Okeanos Explorer CTD Stations *F* and *H* and select WOA13 climatology representative of equatorial source waters for the core (magenta box), with the approximate location of the North Equatorial Current (black arrow), and b) Plot of salinity versus $\Delta N^{deficit}$ (calculated by Eqn. 7) for the select WOA13 data at two latitudes bounding the box, color coded by longitude (note different colorbar scale in Fig. 3a and Fig. 3.b) with station CTD Station ID's also shown beside the colorbar.

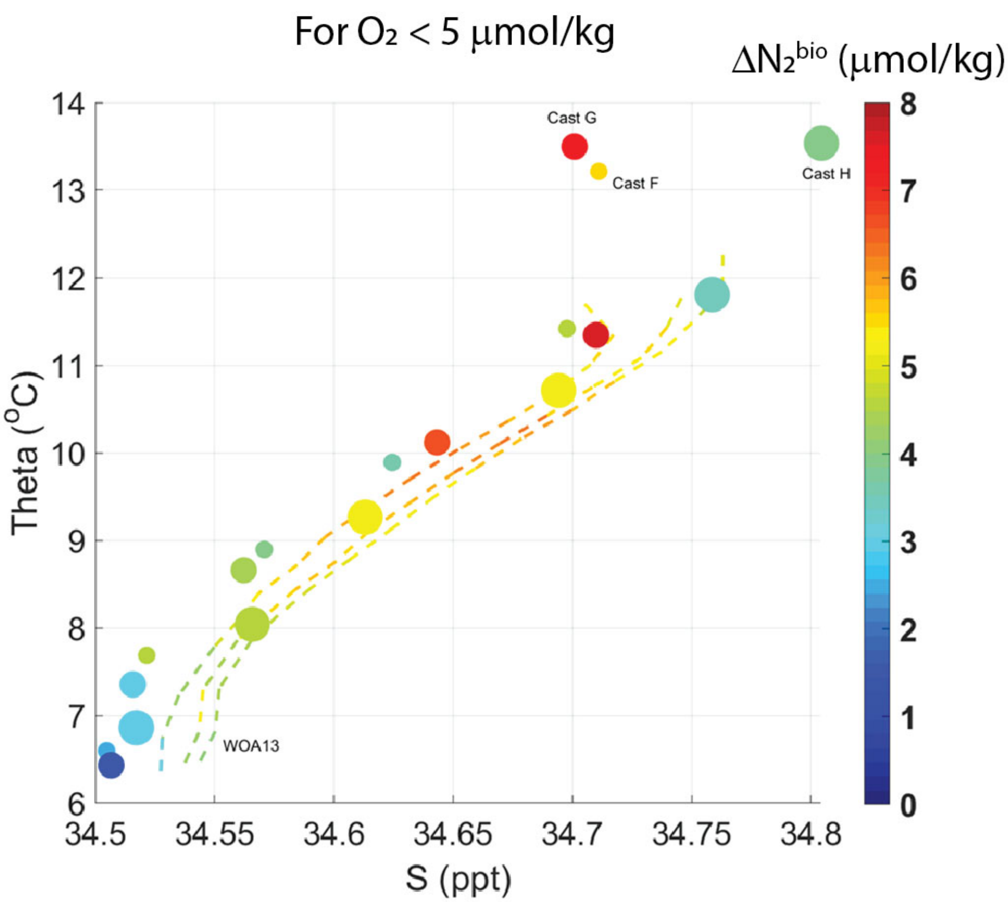

Figure 4. Direct comparison of biogenic N_2 (ΔN_2^{bio}) derived from NOAA Okeanos Explorer nutrient measurements at CTD Stations *F* (small dots), *G* (medium dots) and *H* (large dots) and WOA13 climatology (dashed lines, not uniquely identified since all three lines are very similar).

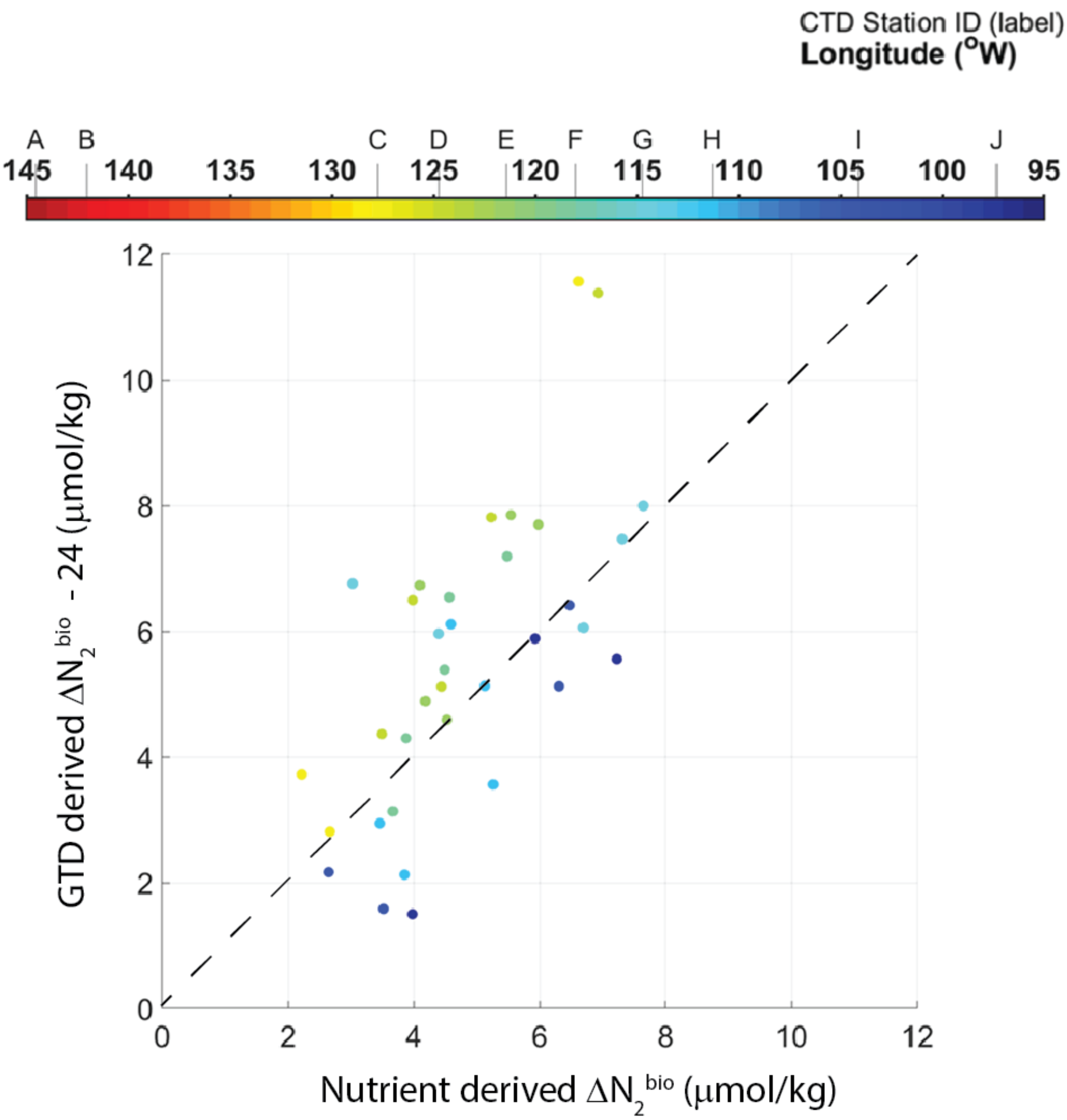

Figure 5. Comparison of biogenic N_2 (ΔN_2^{bio}) estimates derived from NOAA Okeanos Explorer bottle-nutrient measurements and GTD derived estimates offset lower by 24 μmolN_2/kg, color for the ODZ core coded by CTD Station (*A* - *J*). Only measurements near anoxia (O_2 < 5 μmol N_2/kg) are shown and are therefore representative of the ODZ core waters.

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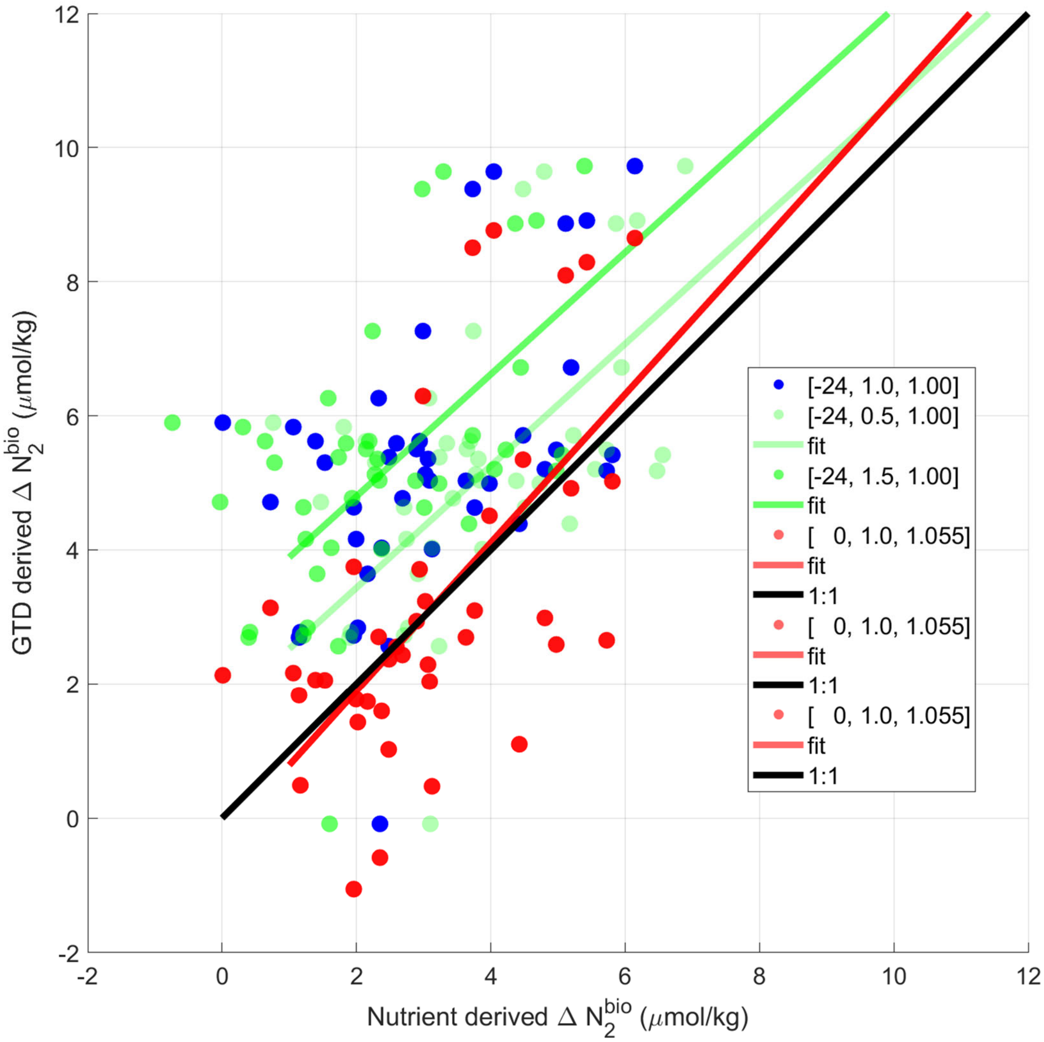

Figure 6. Error analysis of biogenic N_2 estimates from Figure 5, showing variability in the calculations for three variables: [GTD derived biogenic N_2 offset, nitrite gain, argon concentration gain], numerical values are shown in parenthesis in the legend. Also shown are regression fits.