Response to Referee #1

1. *Three different sets of data are used in this study (Time-series data from ALOHA and BATS - for specific locations; WOA 2013 - for basin scales in North Pacific and North Atlantic, and also for world ocean; and GLODAP v2 – for preformed nitrates vs CFC ages of waters) – Comments on comparisons/compatibility among these data sets and their products are worthy of inclusion in the manuscript.*

   We have added text at Lines 177-180 related to this comment: "The WOA and GLODAP data products provide our analysis with an annual time-mean picture of thermocline preNO_3 tracer distributions across the larger spatial scales of the North Atlantic, North Pacific, and the other subtropical gyre regions of the global ocean."

   And at Line 184-185: "All calculations of rNPN and rPPN anomaly formation rates at the time-series sites are performed from analysis of the monthly-resolved Station ALOHA and BATS datasets."

2. *Line 138: for the benefit of the reader it is important to state details of 'total dissolved nitrogen (TDN)' here though available elsewhere. Whether TDN includes PON component or not is unclear from the details provided.*

   We have added text at Lines 170-172 to clarify that samples for TDN are GF/F 0.7 µm filtered and that the time series computed DON concentrations include a negligible amount of ammonium.

3. *Line 183: "DON (measured)" is actually not measured but derived (obtained by difference between TDN and nitrate+nitrite, see lines 140-141).*

   The words "(computed) and (measured)" have been removed from the statement.

4a. Lines 186-191: Assumption of rDOM constancy over time in each density layer may compromise the examination of its temporal variability in the regions. More over near constancy of rDOM values shown in Table 1 for each region might oversimplify vertical variability. If such use is necessary why not consider the top 250 m as just one layer? Please see Comment 16 (a) and (b) below that seem to simplify or play down on actual temporal and spatial variabilities. I am afraid such assumptions may undermine understanding of natural variability and compromise the significance of this study.

Yes, this is an assumption, but necessitated due to the lack of statistically significant AOU vs. DON regressions in a subset of nearly half of the years of data. This is likely because each is a derived tracer subject to measurement and differencing errors. However, our goal of this study is to assess the main causative mechanism for the order of magnitude rPPN/rNPN formation rates we observe, not to report the detailed year-to-year variability of the rPPN/rNPN anomalies. The preformed NO3 anomalies represent a gap in our understanding of the system as the preNO3 tracer computation is meant to remove or account for the effects of biology on observed nitrate distributions. Thus, our goal is to first assess the biological mechanism giving rise to the anomaly before attempting to explain the nuances of its interannual variability. Furthermore, the significance of analyzing a detailed year to year record of rPPN/rNPN anomalies becomes muted when comparing these to the order of magnitude estimates of the contributions from TEP cycling, bacterial NO3 uptake and vertically migrating phytoplankton mechanisms. A detailed study of preNO3 anomaly interannual variability would also likely require a more highly resolved dataset than cruises every 1 – 1.5 months as with the time-series datasets. More detailed float observations as in Johnson et al (2010) will be very helpful in refining these calculations.

4b. Now that authors evaluated rDOM we know the values of rPOM (since DOM and POM remineralization should account for 100% of AOU, see also lines 190-191) specific for ALOHA and BATS. I believe this rPOM will be more realistic. Why use constants of 10.6 and 6.9 from literature? One can make a comparison with literature data but when one has an opportunity to use realistic values one should do so. In the present case the authors seem to prefer using literature values than their own results. Also I am not clear whether the values 10.6 and 6.9 are specific to PON or TON.

Decomposing the AOU into contributions from the remineralization of POM vs. DOM with differing stoichiometry requires 5 parameters: the AOU, fPOM, rPOM, fDOM, and rDOM. The only 2 that can be computed from observed quantities in the HOT and BATS datasets are AOU and rDOM. fDOM and fPOM can be estimated once rDOM is known, by choosing a value of rPOM, and from mass balance that fPOM+fDOM=1. Thus, with the mass balance equation and by prescribing a value of rPOM, one can solve the system of two equations with two unknowns and estimate fDOM and fPOM for the system. Under this constraint, that the value of rPOM must be prescribed, we chose to use the upper bound and lower bound values of rPOM from the literature (the 10.6 and 6.9 values) as a means to test the sensitivity (i.e. to assess the uncertainty) of the computed preNO3 anomalies to this undetermined parameter of our analysis. An observational estimation of rPOM would likely require an oxygen consumption incubation type measurement on field collected sinking POM. These data are unavailable.

5. *Lines 205 – 210: The periods of occurrence of seasonal rNPN and rPPN anomalies and their trends may be shown in x-y plots.*

   These x-y plots are now included in the Supplementary Materials as Figures S1-S5.

6. *Lines 223-225: 'DOM remineralization. . ...that utilizes the preNO3- tracer' is an appreciable observation and suggestion made in this study.*

   We agree. We now use this point and supporting text to begin the Discussion section of the revised manuscript.

7. *Lines 226-230: It appears that 40 to 67% of estimated AOU is explainable by POM oxidation and thus is equally important as that of DOM. Again authors chose to use climatological averages of fDOM than the actual values observed (Comments 2 and 3 are relevant here).*

   We have chosen to use climatological values of fDOM/fPOM in our calculation of preNO3 for the same reasons we discussed in our response to points 4a and 4b. Statistical significance is not present for each year's computation of rDOM leading us to take an approach of a climatological analysis of preNO3 anomalies. Also, we are aiming to assess the main contributing mechanism to rPPN/rNPN anomalies with only order of magnitude estimates to be made for TEP cycling, bacterial NO3 uptake, and vertically migrating phytoplankton with currently available datasets/studies.

8. *Lines 242-245: Are increases in rPPN in the euphotic zone and rNPN in the subsurface waters between May-June and Oct-Nov at ALOHA connected? It should be remembered that we have used near constant values of fDOM (50%), fPOM (50%), rDOM (18.1-18.9) and rPOM of 10.6 or 6.9 in the computations for the entire water column of 200 m (see Table 1). Then the results in Figure 1 are mainly reflective of changes and trends in TDN, Nitrate+Nitrite and Oxygen! I guess results in Figure 1a and b could be different if the authors used their evaluated values of fDOM, fPOM, rDOM and rPOM!!!*

rPPN anomalies in the surface and rNPN anomalies in the subsurface are connected temporally at both stations ALOHA and BATS. This is seen in Figures 1 & 2 but maybe more easily in the newly included Figures S1-S5. There is some degree of temporal offset between the initiation and termination of the two anomalies with rPPN in the surface generally beginning and ending earlier in the calendar year than does rNPN in the subsurface. In the text, we suggest there is a linkage consistent with vertical migrators acquiring nitrate at depth and then reducing it internally to biomass (with oxygen evolution) above the nutricline where nitrate values are vanishingly low (nM). Yes, the reviewer is correct in that because fDOM, fPOM, rDOM, and rPOM are all climatological values in our analysis, the seasonal trends observed in the figures exhibiting residual preNO3 concentrations are reflective of changes in TDN, nitrate+nitrite, and oxygen. As we point out on Line 232-233, the relative uncertainty in the literature values of rPOM is larger (~55%) than the empirically derived rDOM (~33%) variance. Thus, our reported ranges of rNPN and rPPN anomaly formation rates in Table 1 already include a larger estimate of the uncertainty than that which is introduced by using the climatological rDOM and fDOM values from Table 1 in our analysis.

9. *Line 369: "Having ruled out lateral mixing...." This seems to be a very tentative statement since lines 333-335 for BATS and 353-357 ALOHA clearly indicate lateral mixing influence is considerable in deeper layers. Ignoring mixing effects here is not justifiable.*

   Per our analysis, isopycnal mixing may influence the deep rPPN anomaly observed below the euphotic zone >200 m at ALOHA, but it is not a large contributor to the rPPN anomaly at the BATS station or the rNPN anomalies within the lower euphotic zone at either site. We've clarified these points with edited text at Lines 455-456: "This feature is noticeably absent at BATS, (Figure S6) consistent with a minor role for advective mixing there."

   Edits at Line 465-467: "Lateral mixing may explain the observed rPPN anomaly below ~200 m at Station ALOHA: however, the euphotic zone rPPN anomalies and upper mesopelagic zone rNPN anomalies at each site are generated by a local biological mechanism."

10. *Lines 402 and 427: A TEP gradient of 5-10 µg XG eq l-1 was used to assess its contribution to rPPN and rNPN anomalies. I wonder whether such small gradient is sufficient to assessing its role in view of the semi-quantitative nature of TEP measurements and results. The authors should clearly discuss the uncertainties associated with TEP measurements and justify that the gradients used between surface and deep layers are significantly above the analytical errors. Other constraints associated with TEP are identified by the authors in lines 460-465.*

    The reported analytical uncertainty in the studies we cite is 10-13% for µg XG eq L^{-1} which translates to a 3-4 µg XG eq L^{-1} uncertainty on the typically 30 µg XG eq L^{-1} TEP concentration in the upper ocean reported by these studies. Therefore, the TEP gradient we use in our analysis is 1.7 to 3.3 times greater than the analytical uncertainty. By using the published values and assuming they are statistically sound, we have maximized the contribution of TEP. Had we assumed that there was no gradient, the contribution of TEP to the rNPN anomaly would have been much smaller.

11. *Lines 413-414: "We assume TEP is comprised of pure carbohydrate with no N content..." – This is a simplified statement. The TEP has dominant polysaccharide composition but to assume that no other organic materials (nitrogen containing substances) are attached to TEP is not realistic.*

    We had addressed this comment with our text at Lines 466-474 (now Lines 504-514). In our budgeting analysis we used the assumption of no N content in TEP to provide the maximum upper

limit that TEP could contribute to the observed rPPN/rNPN anomalies given the observed upper ocean TEP vertical gradients.

12. *Lines 499-502: ". . .it is clear that neither remineralization of N-poor DOM and TEP or heterotrophic bacterial nitrate uptake can quantitatively explain both the. . ..." – How justifiable is this statement given several assumptions involved. The authors have to quantify uncertainties to give confidence to readers at some level!*

    The uncertainties to our assumptions are what lead to the ranges reported in Table 2. A major source of uncertainty is the value of rPOM (see response to point #8), for which we have chosen to report all of our results as ranges with respect to the lower bound and upper bounds for this value from the literature. In assessing TEP cycling, we have reported its maximum potential contribution based on a theoretical zero N content. Similarly, when assessing bacterial nitrate uptake, we reported its maximum potential contribution based on assigning all bacterial N demand to NO3 uptake when almost certainly a portion is satisfied from remineralization of organic matter. Even with these upper bound estimates of TEP cycling and bacterial NO3 uptake along with the uncertainties in rPOM, etc. we cannot close the residual preNO3 budget at either site, justifying our statement.

13. *Lines 547-550: The logic in the estimation of the contribution of vertically migrating phytoplankton to the rNPN and rPPN ignoring the contribution of physical N transports is not justified (see Comment 9).*

    From our analysis, we did not find large gradients in residual preNO3 necessary for lateral isopycnal mixing to be quantitatively responsible for the observed rPPN and rNPN anomalies above 150 m at BATS and 200 m at ALOHA. Similarly, vertical mixing cannot create the subsurface rNPN anomaly since waters both below and above this layer exhibit positive preNO3 values (from Fig. 1 & 2). The euphotic zone rPPN anomaly cannot be generated from vertical mixing as the waters below exhibit negative preNO3 values. Therefore, we ascribe the remainder of the residual preNO3 anomalies to vertically migrating phytoplankton, our last remaining hypothesized biological mechanism, and compare the anomaly formation rates to vertical nitrate transport rate estimates from the literature.

14. *Lines 557-558 and 564-565 are confusing! When vertically migrating phytoplankton can help explain the observed summertime DIC drawdown in the absence of measurable nitrate (557-558) why do they state 'the mixed layer DIC drawdown need not be entirely supported by migrator photosynthesis, instead their nitrate leakage could help explain. . .(564-565)'. Is not nitrate leaked through excretion used and included in migrator supported photosynthesis?*

    The statement has been edited by removing, "mixed layer DIC drawdown need not be entirely supported by migrator photosynthesis, instead their…". We have also added a new section to the Discussion at Lines 718-756, detailing the potential contribution of the euphotic zone rPPN anomaly formation to the mixed layer DIC drawdown at both sites. We find that the observed seasonal rPPN anomaly can potentially explain a significant fraction (>28%) of the summertime DIC drawdown at each site.

15. *Lines 591-592: "P-limited or P-stressed vertically migrating phytoplankton also take up phosphate at the nutricline. . ." is an important hypothesis.*

    Yes, and we state that this hypothesis can benefit from the collection of field data of vertically migrating phytoplankton intracellular phosphorus concentrations from the subtropical North Atlantic.

16a. SEVERAL ASSUMPTIONS: Lines 186-187: "our approach assumes rDOM is constant over time within each density horizon investigated at each station".

As we have acknowledged, not every year exhibits a statistically significant AOU vs. DON regression to estimate rDOM, diminishing the length and data density of the empirically derived rDOM dataset. We do not observe any trends with time in this dataset.

16b. Lines 202-205: "For the calculation of the preNO3 tracer within the euphotic zone, we made the assumption that the values of fDOM and rDOM were equivalent to those empirically derived for the upper mesopelagic density layer present immediately below the euphotic zone at each site".

This is valid because of our understanding of DOM production and consumption dynamics in the upper ocean. DOM accumulates in the euphotic zone from biological production processes and is subsequently transported vertically to depth, first entering the upper mesopelagic, from physical processes including advection, diffusion, and convection. There, it is remineralized by heterotrophic biological processes. In the absence of large horizontal DOM concentration and DOM stoichiometry gradients (as in the subtropical gyres near stations BATS and ALOHA) and for a system at steady-state on annual timescales, the stoichiometry and magnitude of DOM remineralized in the upper mesopelagic is balanced by that supplied from directly above in the euphotic zone.

16c. Lines 413-414: "We assume TEP is comprised of pure carbohydrate with no N content. . ." – This is probably highly simplified. We know that TEP has dominant polysaccharide composition but to assume that no other organic materials (say proteins etc.) attached to TEP is not realistic.

We had already acknowledged this caveat and how it impacts our results at Lines 466-474 (now Lines 502-514). We agree that it is highly likely there is some N component, either structurally or as attached particles. However, if we assume that TEP contains any % N, we are minimizing the contribution to rNPN. By assuming 0% N, the contribution of TEP is maximum and it makes our conclusion more defensible as maximum values. Any other assumption puts the values somewhere in a poorly defined center.

16d. Lines 453-457 related to assumptions on (i) TEP is pure carbohydrate and (ii) TEP sinks rapidly and account for annual carbon export flux.

We chose these assumptions in our analysis to provide an estimate of the maximum potential contribution for TEP to explain the residual preNO3 formation rates. Actual TEP contribution is likely lower and we stated this at Line 559-560 (now Line 714-715).

16e. Lines 533-535: "Nitrate transport calculations by vertical migration has a number of assumptions and caveats including considerable uncertainty in abundance estimates (Villareal et al., 2014)".

Our statement informs the reader that the largest source of uncertainty in nitrate transport calculations by vertically migrating phytoplankton arise from cell/mat abundance estimates (as detailed in Villareal et al., 2014).

17. *Figure 1 & 2: The captions need clarification. In (a) 'residual pre NO3- tracer' and in (b) 'monthly averaged pre NO3- climatology' have been shown as per the present caption. I wonder if (b) actually shows 'monthly averaged residual pre NO3- tracer climatology'!! If not I would expect different values of higher magnitude of pre NO3- in Figure (b) (according to Formula (1, line 178).*

Yes, we mistakenly left out the word "residual" in the caption to part (b) of Figures 1 & 2. It has been added.

18. *Figure 3: "the residual pre NO3- [μM] tracer (the amount remaining after accounting for DOM contributions to AOU, see lines 233-234)" its maximal value of zero in the world oceans (as shown in this figure) imply that hardly any PON oxidation is accountable for oxygen consumption at 150 m. This sounds unrealistic! (see Comment 7).*

    A value of zero in (now) Fig. 5 means there is no anomaly at 150 m, i.e. POM + DOM remineralization is accurately accounted for by the computation of the preNO3 tracer and there is no significant contribution from TEP, bacterial NO3 uptake, or vertically migration phytoplankton at that location.

19. *Figure S1 & S2: 'Residual pre NO3- is calculated using the values of fDOM and rDOM determined from the BATS station in Table 1 with a value of rPOM = 10.6' – Using fixed BATS values for the entire North Atlantic is not logical as it ignores spatial variability in these values. Figure S1 actually mimics that variability produced by changes in O2 and Nitrate+Nitrite listed in WOA2013!*

    Yes, this is a shortcoming of the mixing analysis arising from low data density in observations of DON across the larger North Atlantic basin, with better spatial coverage in DON data (not available) allowing for a more robust empirical determination of the values of rDON and rDON across the basin. We chose to apply the BATS station empirically derived values of fDOM and rDOM to the larger basin since our goal was to investigate for the presence of large spatial gradients in residual preNO3 distributions within the vicinity of the BATS station on the isopycnals of interest that are needed for lateral mixing to play a quantitatively important role in explaining the observed residual preNO3 distributions at BATS. In Figure S2 (now Fig. S7: plots residual preNO3 on the isopycnal bisecting the rNPN feature at BATS), we observe very little spatial gradient near BATS suggesting insignificant contributions of lateral mixing to the residual preNO3 observed at BATS. Figure S1 (now Fig. S6) plots a slightly deeper isopycnal for the North Atlantic and reveals there is very little vertical gradient comparing residual preNO3 near BATS on isopycnals 26.0 and 26.5, suggesting insignificant contribution from vertical mixing to the rNPN feature within density layer 25.8 – 26.3. Yes, there is likely to be spatial and probably temporal variability in the values of fDOM and rDOM on these isopycnals across the North Atlantic. For example, Carlson et al 2010 DSR II, report values of fDOC in the upper thermocline of the North Atlantic of 5-30%. However, this variability has a minor effect on plotted residual preNO3 concentrations with a change from prescribed fDOM from 0.4 to 0.5 changing the residual preNO3 concentration by < 20% and most typically by < 10% when applied to the WOA dataset for the North Atlantic. Therefore, the evidence suggests that spatial variability in fDOM and rDOM is not large enough to alter our conclusion: that lateral mixing plays an insignificant role in setting the residual preNO3 tracer distribution on the 25.8 – 26.3 isopycnal where seasonal rNPN anomaly formation is observed, with biological mechanisms dominating this process. It is clearly an area that requires more data and we welcome the opportunity to include it in the calculations when available.

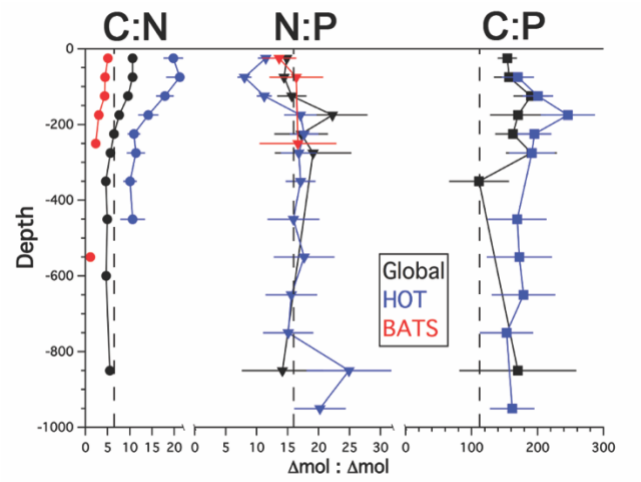
    Figures S3 & S4: See Comment 19 but for North Pacific Ocean.

    See our response to comment 19 which applies to the North Pacific as well. We do recognize that there are larger spatial gradients in residual preNO3 on the deeper 25.4 isopycnal across the North Pacific near station ALOHA which we state could be a significant contributor to the deeper rPPN anomaly observed at >200 m depth within the text at Line 454-455: "Mixing of these waters along γ^n

= 25.4 may explain the observed ~1 µM residual preNO$_3$ concentration present at 200 – 250 m depth in Figure 1."

20. *Figure S5 & S6: Why use Redfield ratio of 16 for N:P here? As the DON gets remineralized the associated phosphate is released in dissolved form. Then why not determine ΔDON/ΔPO4 with time-series data and use that ratio?*

    Author Letscher has previously estimated the ΔDON:ΔDOP ratio in discrete depth intervals at stations ALOHA and BATS (figure adapted from Letscher & Moore 2015, GBC). At BATS (red line), remineralization of the non-refractory (semilabile) DON and DOP in the upper mesopelagic follows a ~16:1 ratio, justifying our use of that ratio here.



22a. Table 2: Lines 133-134 in text: 'Phytoplankton vertical migration. . .. . .at both stations ALOHA and BATS' is not convincing by the information provided in Table 2.

Table 2 has been updated and edited to clarify our approach, results, and conclusions.

22b. It is not clear whether the FOUR sources listed account for 100% of NPN or PPN features listed.

Please refer to our updated Table 2. New rows have been added to show the % contribution of TEP cycling, bacterial NO3 uptake, and vertically migrating phytoplankton to the total observed rNPN or euphotic zone rPPN feature at each site. As is stated in the discussion text, the % contribution from this last process is calculated from the total observed anomaly formation rate minus the contribution from TEP and bacterial NO3 uptake. Therefore, the sum of the three processes sum to 100%. The contribution of N-poor DOM remineralization is not included in the summing to 100% because the main thesis of our study is to quantify and then explain the *residual* preNO3 anomalies present after accounting for DOM remineralization and its stoichiometry to upper ocean AOU budgets.

22c. What are the total NPN and PPN values computed? What about contributions from lateral and vertical/diapycnal mixing, however small they are?

The total rNPN and rPPN values computed are reported in Table 1 as well as within the abstract. We do not include contributions from lateral and diapycnal mixing due to uncertainties in the spatial applicability

of the empirically determined values of fDOM and rDOM to the larger North Atlantic and North Pacific basins as detailed in our response to comments 19 and 20.

22d. Consider all factors/sources and show they account for 100% of NPN or PPN evaluated.

This is now included in our updated Table 2.

22e. Vertical migration appears more significant at BATS than at ALOHA? This will not be clear unless one shows the contributions of various sources in terms of percentage totaling to 100.

This conclusion is more easily gleaned from our updated Table 2.

"Probably a better approach to convince the readers on the significance of nutrient export by phytoplankton vertical migration is by conducting experiments to quantify intracellular accumulation of N and P and the extent of nutrient leakage through excretion by vertically migrating phytoplankton."

This work has been done and is cited in our manuscript. Singler & Villareal 2005 report nitrate, nitrite, and ammonium excretion rates from migrating *Rhizosolenia* mats across the subtropical North Pacific. Villareal & Lipschultz 1995, Villareal et al. 1996, and Woods & Villareal 2008 all document the high (millimolar) intracellular N content of *Rhizosolenia* cells that can only be acquired by direct uptake at µM concentrations, e.g. at the nitracline. Other workers have observed these phenomena in other taxa as well including dinoflagellates including Fraga 2001, Fraga et al 1992, Fraga et al 1999 and Cullen 1985.

Response to Referee #3

1. *That is, the contribution of rNPN and rPPN anomaly formation which is said to be due to vertically migrating phytoplankton are computed by difference of other numbers only – hence there seems to be no direct evidence of the role of migrating phytoplankton to contribute to the subject of this paper (rNPN and rPPN at BAST and HOT, respectively).*

   We have added a header to the last 3 columns of Table 2 entitled, "Proposed attributable process" to better identify these as putative following our analysis. The title of the manuscript has been edited, replacing "Vertically migrating phytoplankton drive" with "Evaluation of the". There is little direct evidence of TEP impact on the rNPN and rPPN anomaly, nor is there direct evidence of heterotrophic nitrate use. We have used the best available data to constrain the contributions of each.

2. *the only evidence seems to be similarity of numbers and the possibility that a process observed and quantified elsewhere (eventually under different hydrographic and biogeochemical conditions?) may exist and dominate also at BATS and HOT. Actually, the two pages (23-24) that summarises very nicely the work of Villareal and others on vertically migrating phytoplankton appear to avoid to mention the locations and conditions of observations related to migrating phytoplankton explicitly.*

   Extensive addition of text has been added at Lines 622-687 to provide a review of the evidence for multiple taxa that are known to be vertical migrators and their meridional/zonal distribution across the global ocean. Multiple vertically migrating phytoplankton taxa have been observed within the vicinity of Station ALOHA and the BATS station. We have included 3 new figures in the Supplementary

Materials detailing the distributions of *Pyrocystis* (Fig. S11), *Ethmodiscus* (Fig. S12), and *Rhizosolenia* (Fig. S13).

3. *I am fine with papers to have a more speculative section. However, this needs to be clearly identified as being speculative, otherwise we leave the scientific ground that facts and clear evidence are the basis of our work.*

   We have updated our language throughout the manuscript when referring to the putative mechanisms with phrases like "potentially explain", "could explain", "proposed mechanism", etc.

4. *Terminology: In the intro you introduce your terms 'residual negative preNO3' (rNPN) and rPPN, respectively. I found the usage of the term residual 'somewhat' misleading, in particularly since the description in M+M is somewhat unrelated to the usage of this term in the intro and in the rest of the paper. Perhaps 'apparent NPN' (etc) is better, particular since rNPN and rPPN rely on a variety of assumptions (fDOM etc.).*

   We have updated throughout the text to ensure that "residual" precedes "preNO$_3$" wherever it is the tracer we refer to. There are some instances in the Intro and Methods in which we mean to refer to preNO$_3$, as in the traditional formulation that is agnostic to differing POM vs. DOM remineralization –O$_2$:N stoichiometry. However, all data presented in the figures, tables, etc. of this study refer to the residual preNO$_3$ tracer which we now clearly define with our edits to the Intro/Methods and edit to Equation 1.

5. *However, I was particularly surprise not to find these terms in M+M! Instead there you use 'traditional preNO3' (l 171) (of which data are never presented, I think) and 'updated calculation' (l 171), initially I wondered whether rNPN is something additional and did not find it well described in M+M. A more clear M+M is required.*

   We have edited this section for clarity such that we clearly define and refer to residual preNO$_3$ as the newly generated tracer data presented in this study including an important edit to Equation 1 which adds the word "residual".

6. *Given the speculative nature of the quantitative role of migrating phytoplankton to the features discussed in this paper, I suggest to delete the last sentence of the Abstract.*

   This statement has been edited as: "These results based on geochemical distributions suggest that in the absence of additional mechanisms and rates, phytoplankton vertical migrators, although rare and easily overlooked, play a larger role in subtropical ocean nutrient cycling and the biological pump than generally recognized."

7. *p 5, l 95 please give a reference for the O2:N ratio; generally, I wonder whether such a low ratio is consistent with the observations of variable elemental ratios in POM (e.g. the work of Martiny et al., but also older work, e.g. Anderson and Sarmiento, 1994, give higher values for –O2:N.)*

   We have added the reference, Anderson, 1995, which updates the POM –O2:N from Anderson and Sarmiento, 1994. The more recent work of Martiny et al. does not specifically address the –O2:C or –O2:N stoichiometry of marine POM, but does provide evidence for regionally variability in POC:PON ratios in the upper ocean. The global mean POC:PON is found to be 6.5 (Martiny et al 2013), i.e. very close to the Redfield value of 6.6. Low latitude oligotrophic regions exhibit elevated C:N closer to 7-7.5.

8. *p5, 106ff: the quote to the Johnson et al 2010 work: do they really suggest what you cite them for? They rather observe a significant amount of Chla below the euphotic zone and argue that these phytoplankton may take advantage of deep nutrient pulses. Thereafter they cite actually earlier work of Villareal in support of upward transport of nitrate by migrating mats. In your intro it sounds as if Johnson provides independent evidence of the migration, which is not the case, I think.*

   We have edited this section for clarity at Lines 122-130: "Johnson et al. (2010) suggested that the subsurface NPN anomaly (calculated using a modified Redfield ratio) could be sustained by vertical separation between nitrate uptake in the nutricline and oxygen production/net community production near the surface. Their data supported the conclusion that the upper 250 m is in approximate balance between nutrient supply and demand, suggesting that there are processes that redistribute nitrate within this region. In the absence of other mechanisms, they suggested that the observed mixed layer net community production is mediated by 1) directly observed episodic vertical physical mixing events that deliver nitrate above 125 m and 2) inferred transport by vertically migrating phytoplankton transporting this nitrate upwards along a near-zero concentration gradient within the euphotic zone."

9. *It might be helpful to mention the two papers of Fraga, which you discuss later, already in the intro*

   Our discussion of the work of Fraga is given within the concluding remarks section at Lines 802-811.

10. ***M+M**, this section is partly confusing, and would benefit from careful reworking*
    -p 8, l 171: 'calculation of the traditional preNO3 tracer', but this is never being used in the results, rephrase please.
    -p7/8, l 173-192: shouldn't this procedure allow to provide error bars for fDOM and rDOM? how large are these? so far, if I understand correctly, the uncertainty in the Tabs mainly derive from literature assumptions about rPOM (10.6 vs. 6.9); how large is the range of rDOM values diagnosed from the data; I see that some of these numbers are provided on p 10 at the beginning of the results section

    The Methods section has undergone extensive editing and reworking, most specifically at Lines 171-185; 198-202; 205-216; 225-236; 247-251; and 258-265.

11. *p9/10, l193-211: I found this part very confusing*

    This section has undergone significant editing at Lines 237-257.

12. *I missed a data availability statement. The time series raw data are available from well known site, but what about the computed data from this study??*

    With the referee's suggestion we have made the residual preNO_3 and residual prePO_4 computed datasets available for the BATS and HOT sites via a supplemental data file to be published with the manuscript.

13. *p 10, l 212: I suggest to add a suppl table with links to the original data used in this study, incl. dates of access, version numbers etc. (TS data, WOA, GLODAP, etc.)*

    We believe that the links listed at Lines 167-177 satisfy this request.

14. *p 10, l 224-226: this is again confusing; do you present results based on the 'traditional preNO3' formulation in this paper?*

    We do not present any "traditional preNO$_3$" tracer concentrations in this study. We have edited text for clarity.

15. *p 11, l 242: I am not sure I really understand how the 'averaged climatology of residual preNO3' is computed; this goes back to the confusion of the M+M section and should be solved there*

    This statement here has been edited to reinforce and restate what is written in the caption for Fig. 1.

16. *p 11, l251: from the text it seems that you sum up the /m3 data of two isopycnals, which can't be right, I think, please clarify*

    This statement has been removed and these values removed from Table 1.

17. *p 12, l 274: really Fig. 1b, not 2b?*

    Yes, this was a mistake. Thank you for catching it.

18. *p 13m 276ff: isn't the similarity of values of rPPN and rNPN an artefact of the way you select rDOM and fDOM for the upper layer (just by adopting it from the lower layer)?*

    No. Because from Equation 1, residual preNO$_3$ still varies as a function of in situ NO$_{3meas}$ and AOU within each depth/density layer investigated.

19. *p 13, l 288/9: You compare /m3 rates (rPPN, rNPN) of different layers and argue that they are balanced. But does that make sence for /m3 values of layers of likely varying thickness?*

    This statement and a similar one at Line 340 have been edited to replace "in approximate balance" with "approximately equivalent".

20. *I suggest to structure the discussion by subheadings*

    Subheadings to the discussion have been added.

21. *p15, l 330: 'Advective mixing' you mean 'lateral mixing', right?*

    Yes. "Lateral" was added.

22. *p15, l 333: reference for CFC data is missing; which kind of age is computed and used here, please provide details*

    Discussion of the methods for CFC diagnosed ventilation age have been added to the Methods at Lines 180-183 including three additional references: "Water mass ventilation ages on subsurface neutral density layers are computed from the GLODAP v2 CFC-11 and CFC-12 data using a method similar to that described in Doney and Bullister (1992) using the atmospheric time-history of the CFC gases provided by Walker et al. (2000) and the gas solubility constants of Warner and Weiss (1985)."

23. *p16, l 354: plots of preNO3 vs. . . ., which preNO3 is given here, the traditional, the improved, the residual?*

    Residual. We have updated throughout the text to ensure "residual" precedes "preNO3" where appropriate.

24. *p 18, l 403-404 (also p19, l 428): the units of the gradient are strange, shouldn't it be ug XGeq /L /m*

    We have replaced "gradient" with "concentration excess".

25. *p 18, 404-413: which physical process mechanism is assumed here, please specify; In general I miss details that feed into the computation in this part*

    We have added text at Line 518-522 to specify the physical mechanisms of sinking of negatively buoyant TEP and/or wintertime vertical mixing: "We take this upper 100 m excess to represent the fraction of the euphotic zone TEP pool that is exported annually to the upper mesopelagic 100-200 m depth layer by a combination of physical sinking of a fraction of the TEP pool that becomes negatively buoyant or is delivered to the subsurface with wintertime vertical mixing."

26. *p 19, 435: the C:-O2 stoichiometry of TEP should be introduced earlier, p 18 or so; eventually in M+M*

    It has been moved up in the Discussion to Line 505.

27. *p 20, l 454-459: this should be given earlier, before you do the computation, e.g. p 18 or so, or eventually in M+M**

    We have moved this section up in the Discussion to Line 500-514 before the discussion of the computation.

28. *p 21, l 467 ff, bacterial N-uptake The underlying assumption is that bacterial biomass is to increase continuously, but aren't the bacteria grazed themselves and the respective N remineralised? I doubt that this process can support NPN anomalies. In particular, the simplistic calculation provided is not convincing and would f.e. require evidence of continuously increasing biomass of bacteria over the growth season that matches the time integrated TEP degradation rates.*

    We have added a statement at Line 594-598 addressing this point: "This proposed mechanism still requires a process that removes bacterial N from the γ^n = 25.8 – 26.3 layer such that a rNPN anomaly is observed due to NO_3 uptake in the absence of stoichiometric O_2 accumulation. Diel vertically migrating grazers are a candidate mechanism whereby grazing on bacterial biomass and its eventual remineralization to NO_3 is spatially separated from respiration and O_2 consumption."

29. *p 23-24: This is a nice summary of evidence for migrating phytoplankton 'somewhere' in the ocean. However, I miss a clear regional and at the same time quantitative link to the topic of this paper: rNPN, rPPN anomalies at BATS and HOT. Statements like ''buoyancy reversals, high internal nitrate pools and rapid ascent have been found in multiple taxa from the Atlantic and Pacific Oceans" (l 530f) or "the generalised rates are consistent with the required rNPN and rPPN rates at BATS and ALOHA" (l 544ff) is much too general.*

Reiteration here of our response to point #2: "Extensive addition of text has been added at Lines 622-687 to provide a review of the evidence for multiple taxa that are known to be vertical migrators and their meridional/zonal distribution across the global ocean. Multiple vertically migrating phytoplankton taxa have been observed within the vicinity of Station ALOHA and the BATS station. We have included 3 new figures in the Supplementary Materials detailing the distributions of *Pyrocystis* (Fig. S11), *Ethmodiscus* (Fig. S12), and *Rhizosolenia* (Fig. S13)."

30. *p 25: l551ff: The authors estimate the contribution of vertically migrating phytoplankton to rNPN and rPPN anomaly features . . . by difference, i.e. as the so far (mechanisms 1, 2, 3) unexplained. This is not sufficient to support a text entitled: "Vertically migrating phytoplankton drive seasonal formation of subsurface negative preformed nitrate anomalies . . ."*

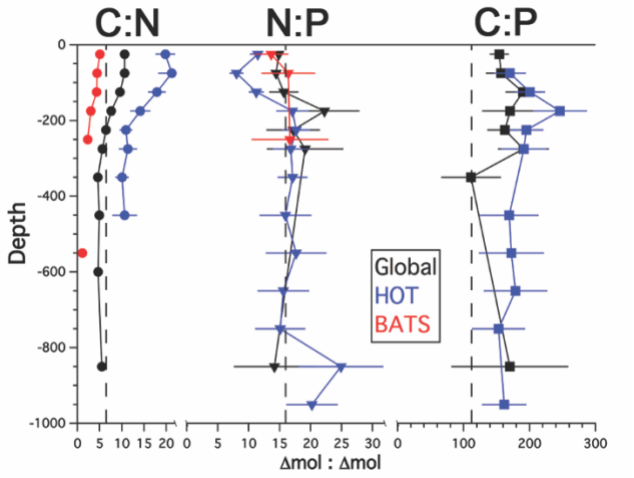
    The title has been changed to remove reference to vertically migrating phytoplankton as the definitive causative mechanism.

31. *p 25, l 561ff (summertime DIC drawdown): again, this is highly speculative since you do not provide sound numbers for the role of vertically migrating phytoplankton for the two time series stations, based on data from the sites*

    Our language in this section had reflected this as speculative, using phrases including "can help explain", "can lead to", "could help explain".

32. *p 26, l 575ff: Preformed PO4 is a very important aspect of the paper; I suggest to present the respective data already in the results section and with the same rigor as the rNPN etc data. You can discuss / provide the interpretation her in the discussion, of course. Questions arise: You assume that fDOM and rDOM are the same for DOP and DON, due to lack of data, as you point out. However, this make the analysis a very weak one, I think. DOP and DON differ in their composition, shouldn't they also differ in their contribution to AOU, accordingly?*

    We have performed the suggestion and created new Figures 3 and 4, which replace Figures S5 and S6. Residual preformed PO4 is now defined in the Methods at Lines 258-265 and discussed in the Results at Lines 347-370 and the Discussion at Lines 757-784. We now cite our previous study justifying our prescribed rDOM value for the calculation of residual prePO4 which uses a semilabile DON:DOP remineralization stoichiometry of 16:1 (Letscher & Moore, 2015 GBC), adapted figure provided below.



33. *p 27, 596ff: is there direct evidence for phosphate transport via migrating phytoplankton (at least from other sites); in which form is PO4 stored in the cells?*

    We have added text at lines 779-784: "Limited sampling in the waters between Hawai'i and California indicated N:P ratios were not significantly different between sinking and ascending *Rhizosolenia* mats (N:P ~26-30) while C:P ratios were significantly different (p = 0.05, C:P sinkers = 388 ± 66; C:P ascending = 221 ± 43). This is consistent with simultaneous uptake of N and P at depth, but carbon consumption at depth relative to the surface. Further data on phosphate composition of vertically migrating phytoplankton are needed to confirm our hypothesis."

34. *p27, l 600: I think your conclusions start here. Perhaps use a respective section title?*

    Yes, we now have added a section title beginning here, "Concluding Remarks".

35. *p 28: l 622: "to confirm the conclusion" " confirm the hypothesis"*

    This change has been made.

36. *p 28, l 622: " multiple authors": give at least some references*

    We have added four references to this statement: Cullen, 1985; Richardson et al 1998; Fraga, 2001; Villareal et al 2014.

Evaluation of the seasonal formation of subsurface negative preformed nitrate anomalies in the subtropical North Pacific and North Atlantic

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Abstract

Summertime mixed-layer drawdown of dissolved inorganic carbon in the absence of measurable nutrients in the ocean's subtropical gyres and non-Redfieldian oxygen:nitrate relationships in the underlying subsurface waters are two biogeochemical phenomena that have thus far eluded complete description. Many processes are thought to contribute to one or both including lateral nutrient transport, carbon overconsumption or non-Redfield C:N:P organic matter cycling, heterotrophic nutrient uptake, and the actions of vertically migrating phytoplankton. To obtain insight into the likely magnitude of potential contributing mechanisms, we investigated the seasonal formation rates for negative preformed nitrate ($preNO_3$) anomalies (oxygen consumption without stoichiometric nitrate release) in the subsurface and positive preformed nitrate anomalies (oxygen production without stoichiometric nitrate drawdown) in the euphotic zone at the subtropical ocean time series stations ALOHA in the North Pacific and BATS in the North Atlantic. Non-Redfield $-O_2$:N stoichiometry for dissolved organic matter (DOM) remineralization is found to account for up to ~15 mmol N m^{-2} yr^{-1} of negative $preNO_3$ anomaly formation at both stations. Residual negative anomalies in excess of that which can be accounted for by non-Redfield DOM cycling are found to accumulate at a rate of ~32 – 46 mmol N m^{-2} yr^{-1} at station ALOHA and ~46 – 87 mmol N m^{-2} yr^{-1} at the BATS station. These negative anomaly formation rates are in approximate balance with residual positive $preNO_3$ anomaly formation rates from the euphotic zone located immediately above the nutricline in the water column. Using the limited literature available, we calculate that cycling of transparent exopolymer particles (TEP) and heterotrophic nitrate uptake can contribute to the formation of these residual $preNO_3$ anomalies; however, a significant fraction, estimated at ~50 – 95%, is unexplained by the sum of these processes. Vertically migrating phytoplankton possess the

necessary distribution, nutrient acquisition strategy and biogeochemical signature to potentially explain both the negative and positive residual $preNO_3$ anomalies as well as the mixed layer dissolved inorganic carbon drawdown at stations ALOHA and BATS. However, the processes examined are not independent and mutually exclusive. The model *Rhizosolenia* mat system (and perhaps other migrators) produce TEP and migration could provide accelerated vertical transport of TEP as well as provide labile carbon for heterotrophic nitrate uptake. These results based on geochemical distributions suggest that in the absence of additional mechanisms and rates, phytoplankton vertical migrators, although rare and easily overlooked, play a larger role in subtropical ocean nutrient cycling and the biological pump than generally recognized.

Introduction

Subtropical ocean gyre ecosystems exhibit low rates of primary productivity caused by thermal stratification of the water column that acts as an impediment to sustained nutrient supply to the surface ocean. Yet these regions exhibit significant annual net community production (ANCP), estimated at 3 ± 1 mol C m^{-2} yr^{-1} for station ALOHA in the North Pacific (Hawaii Ocean Time-series) and the BATS station (Bermuda Atlantic Time-Series) in the North Atlantic (Emerson, 2014), contributing about half of the global biological carbon pump (Emerson et al., 1997). Observations at these two well-characterized time-series sites indicate a seasonal drawdown of mixed layer dissolved inorganic carbon (DIC) occurs during the summer and early autumn months that is attributed to net community production with minor contributions from lateral mixing and air-sea CO_2 exchange (Gruber et al., 1998, 2002; Keeling et al., 2004; Williams et al., 2013).

The nutrient sources supporting this seasonal DIC drawdown at the time-series sites have eluded oceanographers since the phenomenon was first documented (Michaels et al., 1994; Toggweiler, 1994; Gruber et al., 1998; Keeling et al., 2004). Numerous nutrient input mechanisms have been investigated including vertical mixing, N_2 fixation, atmospheric deposition, and eddy movements with their sum still falling short of explaining the observed DIC drawdown or a stoichiometric equivalent subsurface oxygen consumption (Jenkins and Goldman, 1985; Jenkins and Doney, 2003) assuming Redfield stoichiometry between organic matter production and remineralization. More recently, episodic vertical mixing events and lateral advection are two physical mechanisms that have been proposed to supply the surface subtropical gyres with the "missing" nutrients to explain observed ANCP (Johnson et al., 2010; Letscher et al., 2016). However, in order to explain the observed summertime DIC drawdown from the subtropical gyre mixed layer, these two physical mechanisms must supply nutrients, carbon, and oxygen in non-Redfield stoichiometries. Letscher et al. (2016) reported C-deficient, non-Redfieldian supply of inorganic carbon and nutrients within the lateral nutrient streams reaching the subtropical gyres; however, this mechanism still falls short of explaining the observed DIC drawdown at stations ALOHA and BATS, even after accounting for non-Redfield C:N:P stoichiometry of organic matter production. Johnson et al. (2010) used profiling floats equipped with biogeochemical sensors to observe episodic, near monthly, vertical mixing events near station ALOHA that supply nitrate from the nitracline upwards into the euphotic zone to a depth of ~75-100 m. To explain the surface DIC drawdown, these authors suggested the non-Redfieldian supply of nitrate into the mixed layer above ~50 m could be carried out by large, non-flagellated phytoplankton that migrate between the nutricline and the surface as part of their life-history strategy for nutrient acquisition (Villareal et al., 1993; 2014). Multiple lines of

evidence indicate that this subset of the oceanic flora is migrating (Villareal et al., 2014) and transports new nitrogen into the euphotic zone (Villareal et al., 1993; Richardson et al., 1998; Villareal et al., 1996). As an analogy, migration by flagellated phytoplankton in coastal waters is sufficient to alter geochemical properties. Fraga et al. (1992, 1999) observed that the flagellated coastal dinoflagellate *Gymnodinium catenatum* transports nutrients via vertical migration in relaxed upwelling conditions and developed modifications to Broeker's (1974) NO tracer that expressed how the dinoflagellate migration modifies geochemical properties. In the open ocean, giant phytoplankton (up to 10^9 μm^3) can overcome the much greater distances (~50–100 m) required to access the spatially segregated resource fields (light and nutrients) with size related ascent and descent rates. The challenge has been to quantify the various taxa's role in nitrate transport since this group is difficult to enumerate and abundance data is quite limited (Villareal et al., 2014).

In conjunction with the "missing" nutrient supply required to explain observed mixed layer DIC drawdown, the subtropical gyre regions also exhibit a deficit of sub-euphotic zone nitrate as expected from observed oxygen consumption and Redfield $-O_2$:N organic matter remineralization stoichiometry. This phenomenon is revealed when examining spatiotemporal patterns of the preformed nitrate ($preNO_3$) tracer. $preNO_3$ is traditionally calculated as $preNO_3 = NO_{3meas} - AOU/R_{-O2:N}$, where AOU is the apparent oxygen utilization and $R_{-O2:N}$ is the stoichiometric ratio of oxygen consumed to N regenerated for the remineralization of Redfieldian organic matter, e.g. 150:16 (9.4; Anderson, 1995). $preNO_3$ quantifies the fraction of measured nitrate in a water parcel not attributable to remineralization of Redfieldian organic matter and was initially formulated as a conservative tracer for examining the distribution of water masses involved in the global thermohaline circulation (Broecker, 1974). However, observations of

115 preNO$_3$ within upper mesopelagic depths (~100-300 m) of the subtropical ocean have revealed
116 negative preNO$_3$ (NPN) anomalies, suggesting there are non-Redfieldian processes affecting the
117 *in situ* dissolved oxygen and nitrate pools as well (Abell et al., 2005; Johnson et al., 2010). That
118 is, the observed negative anomalies are the result of oxygen consumption without concurrent
119 Redfieldian nitrate accumulation. Abell et al. (2005) suggested production, export, and
120 remineralization of dissolved organic matter (DOM) with non-Redfield, elevated C:N
121 stoichiometry could quantitatively explain the subsurface preNO$_3$ distribution in the subtropical
122 North Pacific. Working in the same ecosystem, Johnson et al. (2010) suggested that the
123 subsurface NPN anomaly (calculated using a modified Redfield ratio) could be sustained by
124 vertical separation between nitrate uptake in the nutricline and oxygen production/net
125 community production near the surface. Their data supported the conclusion that the upper 250
126 m is in approximate balance between nutrient supply and demand, suggesting that there are
127 processes that redistribute nitrate within this region. In the absence of other mechanisms, they
128 suggested that the observed mixed layer net community production is mediated by 1) directly
129 observed episodic vertical physical mixing events that deliver nitrate above 125 m and 2)
130 inferred transport by vertically migrating phytoplankton transporting this nitrate upwards along a
131 near-zero concentration gradient within the euphotic zone. Additional hypotheses advanced to
132 explain the DIC drawdown and/or the subsurface NPN anomaly include heterotrophic uptake of
133 nitrate and spatially segregated transparent exopolymer (TEP) production and consumption. To
134 date, no work has attempted to partition the contribution of the various mechanisms to formation
135 of the negative preNO$_3$ anomaly in subtropical ocean gyre systems.

136 In this work, we expand the examination of preNO$_3$ anomalies to the BATS station in the
137 North Atlantic and revisit the missing nutrient and NPN anomaly problems at both stations

ALOHA and BATS. We update the calculation of $preNO_3$ to explicitly include the contribution of DOM and its non-Redfield $-O_2$:N remineralization stoichiometry to the subsurface tracer fields in a manner analogous to Abell et al. (2005). Using this revised $preNO_3$ calculation, we define the residual $preNO_3$ tracer, which quantifies the $preNO_3$ distribution not attributable to the non-Redfield $-O_2$:N DOM remineralization stoichiometry mechanism. Seasonal formation of a sub-euphotic zone residual negative $preNO_3$ (rNPN) anomaly at the BATS station and a persistent sub-euphotic zone rNPN anomaly at station ALOHA are identified within the nutricline, similar to previous work in the subtropical North Pacific (Abell et al., 2005; Johnson et al., 2010). In addition, residual positive $preNO_3$ (rPPN) anomalies are observed within the euphotic zone (0 – ~80 or ~100 m) at both sites, with integrated rates of formation that are in approximate stoichiometric balance with the rNPN anomalies located immediately below in the water column. These rNPN and rPPN anomalies account for the effects of both particulate organic matter (POM) and DOM remineralization with elevated $-O_2$:N stoichiometry, thus requiring additional mechanisms for their formation. We undertake a quantitative examination of other potential contributing mechanisms to explain the subsurface rNPN anomalies, euphotic zone rPPN anomalies, and mixed layer DIC drawdown including transparent exopolymer particle (TEP) cycling, subsurface bacterial uptake of nitrate, and vertical migration by phytoplankton. We find that TEP cycling may explain a fraction of both the rNPN and rPPN anomalies; bacterial nitrate uptake accounts for only a small fraction of rNPN and none of the rPPN anomalies. In the absence of additional unknown mechanisms, phytoplankton vertical migration contributes the dominant flux of N to explain both the rNPN (via nitrate consumption and upward transport) and rPPN (via oxygen production during internal nitrate consumption) anomalies at both stations ALOHA and BATS. The observed rates at the time-series sites are within the range of previously

estimated vertical transport rates elsewhere in the subtropical ocean. In addition, the observed production of TEP by migrating diatom mats (and by inference, other migrators) provides a linkage between at least two of the processes. These calculations provide a framework for evaluating the role of these processes in future studies.

Methods

Data

Time-series biogeochemical data including concentrations of total dissolved nitrogen, nitrate + nitrite, and oxygen for the years 1988-2016 were downloaded from http://bats.bios.edu for the BATS station and http://hahana.soest.hawaii.edu/hot for Station ALOHA. Dissolved organic nitrogen (DON) was calculated as total dissolved nitrogen (GF/F 0.7 µm filtered) minus [nitrate + nitrite]. This definition of DON includes ammonium; however, its open ocean concentration is typically < 50 nM and is not regularly measured as part of the two time-series. Global annual climatologies for dissolved O_2 and NO_3^- from the World Ocean Atlas (WOA) 2013 (Garcia et al., 2014a; 2014b) were downloaded from http://www.nodc.noaa.gov/OC5. The Global Ocean Data Analysis Project (GLODAP) v2 dataset (Olsen et al. 2016) including dissolved O_2, NO_3^-, CFC-11, and CFC-12 was downloaded from http://www.nodc.noaa.gov/ocads/oceans/GLODAPv2. The WOA and GLODAP data products provide our analysis with an annual time-mean picture of thermocline preNO_3 tracer distributions across the larger spatial scales of the North Atlantic, North Pacific, and the other subtropical gyre regions of the global ocean. Water mass ventilation ages on subsurface neutral density layers are computed from the GLODAP v2 CFC-11 and CFC-12 data using a method similar to that described in Doney and Bullister (1992) using the atmospheric time-history of the CFC gases

provided by Walker et al. (2000) and the gas solubility constants of Warner and Weiss (1985). All calculations of rNPN and rPPN anomaly formation rates at the time-series sites are performed from analysis of the monthly-resolved Station ALOHA and BATS datasets.

Tracer computations

The preformed NO_3 tracer defined by Broecker (1974) separates the observationally determined nitrate concentration for a given water parcel into contributions from water mass mixing (preformed) and regenerated from respiration of organic matter. Traditional formulations of preNO_3 assign a uniform $-O_2$:NO_3 stoichiometry, e.g. 9.0 (Broecker, 1974), of organic matter remineralization without discriminating between particulate vs. dissolved organic matter (DOM) pools. However, Abell et al. (2005) showed that DOM remineralization stoichiometry is significantly elevated with respect to Redfield proportions in the subtropical North Pacific, with $-O_2$:N stoichiometries of 23 to 30 within shallow mesopelagic density layers (σ_θ = 24.4 – 26.1) compared to Redfield values of 6.9 to 10.6 (Takahashi et al., 1985; Martin et al., 1987; Anderson and Sarmiento, 1994; Paulmier et al., 2009). This required an additional term in the calculation of preNO_3 in their analysis, accounting for the fraction of oxygen consumption attributable to DOM remineralization and its separate stoichiometry. Abell et al. (2005) inferred the subsurface $-O_2$:N stoichiometry of DOM remineralization from regressions of observed O_2 vs. dissolved organic carbon (DOC) concentrations within upper mesopelagic isopycnal layers. The regression was converted to N units with the separately measured DOC:DON ratio. Here we adopt the Abell et al. (2005) analysis and directly estimate the $-O_2$:N stoichiometry of dissolved organic nitrogen remineralization within upper mesopelagic density layers at stations ALOHA and BATS to compute the residual preNO_3 tracer.

The residual $preNO_3$ tracer formulation including the effects of DOM remineralization is:

$$residual\ preNO_3 = NO_{3meas} - \left(f_{DOM} \cdot \frac{AOU}{rDOM}\right) - \left(f_{POM} \cdot \frac{AOU}{rPOM}\right) \quad (1)$$

NO_{3meas} is the sum of dissolved nitrate + nitrite. Apparent oxygen utilization (AOU) is calculated as $AOU = O_{2sat} - O_{2meas}$; the difference between O_2 saturation at a given temperature, salinity, and pressure with the observationally determined O_2 concentration. The two DOM terms, f_{DOM}, the fraction of oxygen consumption attributable to DOM remineralization and r_{DOM}, the stoichiometric ratio of O_2 consumed per mole of DON remineralized, can be determined empirically from the time-series O_2 and DON data. Values of r_{DOM} were determined empirically each year between 1989 – 2000 at Station ALOHA and 1993 – 2016 at the BATS station by Model II linear regression (Ricker, 1973; Trujillo-Ortiz and Hernandez-Walls, 2010) of AOU vs. DON within discrete neutral density layers. The subsurface neutral density layers $\gamma^n = 24.2 – 24.7$ and $\gamma^n = 24.7 – 25.2$ were chosen at station ALOHA and $\gamma^n = 25.8 – 26.3$ at the BATS station for subsequent calculation of DOM $–O_2$:N remineralization stoichiometry based on a first examination of the depths exhibiting NPN anomalies using the traditional (Redfieldian) formulation of the $preNO_3$ tracer, i.e. $preNO_3 = NO_{3meas} – AOU/R_{-O2:N}$. with the value of $R_{-O2:N}$ selected as 150:16 (Anderson, 1995). The fraction of oxygen consumption attributable to DOM remineralization, f_{DOM}, is determined empirically for each neutral density layer following the equation of Abell et al. (2000):

$$f_{DOM} = \frac{\Delta DOM}{\Delta DOM + \Delta POM} = \frac{rPOM}{rDOM} \quad (2)$$

The stoichiometric ratio of O_2 consumed per mole of particulate organic nitrogen (PON) remineralized, r_{POM}, cannot be uniquely determined from Eq. 2 or the time-series data and is taken from the literature (6.9 to 10.6; Paulmier et al., 2009). We used the climatological average r_{DOM} in Eq. 2 due to a reduced number of years exhibiting statistically significant regressions of

AOU vs. DON. Years with a regression correlation coefficient > 0.33 were included in the climatological average (~55% of years investigated). Thus, our approach assumes r_{DOM} and f_{DOM} are constant over time within each density horizon investigated at each station. Relative uncertainty in the literature values of r_{POM} is larger (~55%) than the computed uncertainty in r_{DOM} (~33%). The last remaining term in Eq. 1, f_{POM}, the fraction of AOU attributable to POM remineralization, is calculated as $1 - f_{DOM}$. We tested the sensitivity of our computed residual $preNO_3$ from Eq. 1 and 2 by allowing r_{POM} to vary from 6.9 to 10.6, the upper and lower bound values for r_{POM} reported in the literature (Paulmier et al., 2009).

The seasonal formation rate of rNPN anomalies at each time-series site were estimated by a linear regression of the residual $preNO_3$ tracer vs. time within the aforementioned subsurface neutral density layers for the years 1989-2016 at Station ALOHA and 1993-2016 at the BATS station. The slope of this regression yields the volumetric rate of rNPN anomaly formation in units of μmol N m^{-3} d^{-1}. The volumetric rates were depth and time integrated to provide annual rates of rNPN anomaly formation in units of mmol N m^{-2} yr^{-1}. Depth integration was performed by estimating the thickness, H, each year of the subsurface neutral density layers at the BATS and ALOHA stations. Values of H varied between 20 to 100 m. Time integration was calculated from the number of days elapsed between the first observation of decreasing residual $preNO_3$ values to the date when residual $preNO_3$ ceased decreasing within the annual cycle (Fig. S1, S2, S4). The volumetric rates of rPPN formation within the euphotic zone and their depth integration at each time-series site were performed within the 0 – 100 m layer at Station ALOHA and within the 0 – 80 m layer at the BATS station. Time integration for rPPN anomalies was performed analogously to rNPN anomalies; from the time elapsed between observations of increasing residual $preNO_3$ within the euphotic zone over the annual cycle (Fig. S3, S5). For the calculation

of the residual $preNO_3$ tracer within the euphotic zone, we made the assumption that the values of f_{DOM} and r_{DOM} were equivalent to those empirically derived for the upper mesopelagic density layer present immediately below the euphotic zone at each site. Seasonal rNPN anomaly formation duration ranged from a minimum of 2 months to a maximum of 10.5 months with a median of 7.5 months. Seasonal rPPN anomaly formation duration ranged from a minimum of 4 months to a maximum of 10 months with a median of 6 months.

A residual preformed phosphate ($prePO_4$) tracer was computed as:

$$residual\ prePO_4 = PO_{4meas} - \left(f_{DOM} \cdot \frac{AOU}{rDOM}\right) - \left(f_{POM} \cdot \frac{AOU}{rPOM}\right)$$

Dissolved organic phosphorus concentration data density was not sufficient to allow for statistically significant regressions of AOU versus DOP needed to empirically estimate f_{DOM} and r_{DOM} terms specific to DOP remineralization at each site. To compute $prePO_4$ for each station, we used the values of f_{DOM}, r_{DOM}, and r_{POM} from Table 1 calculated from regressions of AOU vs. DON, converting from N units to P units using a DON:DOP ratio of 16:1 for semilabile DOM remineralization in the subtropical North Atlantic and North Pacific (Letscher & Moore, 2015).

Results

DOM remineralization in the upper mesopelagic at the ALOHA and BATS stations

Empirically derived, annual values of r_{DOM} at Station ALOHA varied between 10.4 and 24.2 for the γ^n = 24.2 – 24.7 layer and between 12.7 and 23.5 for the γ^n = 24.7 – 25.2 layer. Values of r_{DOM} at the BATS station varied between 14.0 and 25.3 in the γ^n = 25.8 – 26.3 layer. Climatological average r_{DOM} computed for each density layer yielded ratios of 18.1 to 18.9 at Station ALOHA and 21.1 at the BATS station (Table 1; standard errors on r_{DOM} are on the order of 33%). These climatological values of r_{DOM} were used in subsequent calculations of residual

preNO$_3$ and f_{DOM} from equations 1 and 2. The empirically derived values of r_{DOM} are consistently larger than the literature estimates of r_{POM}, indicating that remineralization of DOM in the upper mesopelagic returns less moles of nitrate per mole of O_2 respired at the two sites compared to Redfield stoichiometry.

Empirically derived values of f_{DOM} varied between 0.38 and 0.59 for the γ^n = 24.2 – 24.7 layer and between 0.36 and 0.6 for the γ^n = 24.7 – 25.2 layer at station ALOHA. Values of f_{DOM} at the BATS station varied between 0.33 and 0.5 in the γ^n = 25.8 – 26.3 layer. Climatological average f_{DOM} values of 0.5 for both density layers at station ALOHA and a value of 0.4 at the BATS station (Table 1) were used in subsequent calculation of residual preNO$_3$ from Equation 1.

Upper ocean residual preNO$_3$ climatology at the ALOHA and BATS stations

Station ALOHA – The climatology of the residual preNO$_3$ [µM] tracer (the amount remaining after accounting for DOM contributions to AOU) is presented for the upper 250 m at Station ALOHA in Figure 1a. Residual preNO$_3$ varies between -1 to 1 µM in the upper ~200 m with increasingly positive values below 200 m. The resulting rNPN anomaly (blue colors) is a persistent feature within the 24.2 – 25.2 neutral density layer at a depth of ~100 to 200 m. Seasonal rPPN anomalies (red colors) are observed immediately above the 24.2 neutral density horizon within the euphotic zone, 0 to ~100 m. Pulses of rPPN anomalies penetrating the bottom of the rNPN anomaly layer are also observed that coincide with shoaling of the 25.2 neutral density horizon above 200 m.

The monthly averaged climatology of residual preNO$_3$ [µM] at Station ALOHA for all data in years 1989 – 2016 is presented in Figure 1b. The subsurface rNPN anomaly is observed to grow in magnitude between the months of May/June through Oct/Nov. There also exists an

increase in the magnitude of the rPPN anomaly within the euphotic zone (0 – 100 m), concomitant with the rNPN anomaly formation at ~100 – 200 m depth in summer.

Volumetric rates of rNPN anomaly formation at Station ALOHA are estimated at 2.8 ± 1.4 and 3.0 ± 1.5 μmol N m^{-3} d^{-1} for the γ^n = 24.2 – 24.7 layer using r_{POM} values of 6.9 and 10.6, respectively (Table 1). Slightly lower rates of rNPN anomaly formation of 1.6 ± 0.8 and 2.5 ± 1.4 μmol N m^{-3} d^{-1} are estimated for the deeper γ^n = 24.7 – 25.2 layer at Station ALOHA (annual regressions are provided in Fig. S1 & S2). Depth and time integrated, the estimates of rNPN anomaly formation become 28.3 ± 9.6 (r_{POM} = 6.9) and 17.9 ± 7.4 (r_{POM} = 10.6) mmol N m^{-2} yr^{-1} for the γ^n = 24.2 – 24.7 layer and 18.1 ± 8.8 (r_{POM} = 6.9) and 13.7 ± 7.8 (r_{POM} = 10.6) mmol N m^{-2} yr^{-1} for the deeper γ^n = 24.7 – 25.2 layer. Total rNPN formation rate estimates for Station ALOHA are between 31.6 ± 10.8 to 46.4 ± 13.0 mmol N m^{-2} yr^{-1} (Table 1).

The volumetric rate of rPPN anomaly formation within the euphotic zone at Station ALOHA is estimated at 3.3 ± 1.1 and 2.4 ± 0.8 μmol N m^{-3} d^{-1} using r_{POM} values of 6.9 and 10.6, respectively (Table 1, Fig. S3). These rates are approximately equivalent within error of those estimated for rNPN formation rate within the γ^n = 24.2 – 24.7 layer immediately below in the water column. Depth and time integrated, the estimate of rPPN anomaly formation is 61.2 ± 20.2 (r_{POM} = 6.9) and 43.5 ± 10.5 (r_{POM} = 10.6) mmol N m^{-2} yr^{-1} (Table 1). The euphotic zone integrated rPPN anomaly is approximately 33% higher than the estimated total integrated rNPN anomaly within the combined γ^n = 24.2 – 25.2 layer.

BATS – The climatology of the residual $preNO_3$ [μM] tracer in the upper 200 m at BATS is presented in Figure 2a. Residual $preNO_3$ varies between -1 to 1 μM in the upper 200 m and seasonal subsurface rNPN anomalies at ~80 to 160 m depth are observed in most but not all years from 1993 to 2016. Similar to Station ALOHA, seasonal pulses of rPPN anomalies are

observed immediately above the 25.8 neutral density horizon within the euphotic zone, 0 to ~80 m. Pulses of rPPN anomalies penetrating from below the 26.3 neutral density horizon are present in a few years but are much less frequent than observed in the Station ALOHA climatology. rPPN anomalies are observed immediately below the rNPN layer beginning at ~160 m.

The monthly averaged climatology of residual preNO$_3$ [µM] at BATS for all data in years 1993 – 2016 is presented in Figure 2b. The subsurface rNPN anomaly is observed to first appear beginning in Apr/May and grow in magnitude through the end of the calendar year. The rNPN feature starts shallow at a depth of ~60 to 100 m that deepens over the summer months to depths of ~80 to 160 m by years' end. There also exists a layer of rPPN anomaly at 0 – ~80 m depth that increases in magnitude, concomitant with the rNPN anomaly formation at ~80 – 160 m depth in summer and autumn. Late winter convective overturn of the upper water column in late Jan/Feb at the BATS station (Hansell and Carlson, 2001) erases both the subsurface rNPN and 0-80 m rPPN anomaly.

The volumetric rate of rNPN anomaly formation at the BATS station is estimated at 5.5 ± 2.7 and 3.8 ± 3.1 µmol N m^{-3} d^{-1} for the γ^n = 25.8 – 26.3 layer using r_{POM} values of 6.9 and 10.6, respectively (Table 1, Fig. S4). Depth and time integrated, the estimate of rNPN anomaly formation rate at the BATS station is between 46.0 ± 39.3 to 87.1 ± 41.0 mmol N m^{-2} yr^{-1} (Table 1). The volumetric rate of rPPN anomaly formation within the euphotic zone at the BATS station is estimated at 5.8 ± 1.2 and 4.1 ± 0.8 µmol N m^{-3} d^{-1} using r_{POM} values of 6.9 and 10.6, respectively (Table 1, Fig. S5). These rates are approximately equivalent within error of those estimated for rNPN formation rate within the γ^n = 25.8 – 26.3 layer immediately below in the water column. Depth and time integrated, the estimate of rPPN anomaly formation is 82.1 ± 13.8 (r_{POM} = 6.9) and 61.8 ± 12.2 (r_{POM} = 10.6) mmol N m^{-2} yr^{-1} (Table 1). The euphotic zone

integrated rPPN anomaly is approximately balanced (r_{POM} = 6.9) or 33% higher (r_{POM} = 10.6) than the estimated integrated rNPN anomaly within the γ^n = 25.8 – 26.3 layer.

Upper ocean residual $prePO_4$ climatology at the ALOHA and BATS stations

Station ALOHA – The climatology of the residual $prePO_4$ [µM] tracer is presented for the upper 250 m at Station ALOHA in Figure 3a. Residual $prePO_4$ varies between -0.04 to 0.2 µM with positive values observed throughout the upper 250 m of the time-series with exception of a period exhibiting small (~0 – -0.04 µM) residual negative $prePO_4$ anomalies at ~125 – 175 m in years 2002 – 2004. The monthly averaged climatology of residual $prePO_4$ [µM] at Station ALOHA for all data in years 1989 – 2016 is presented in Figure 3b. Positive residual $prePO_4$ (0 – 0.2 µM) is observed throughout the upper 250 m within the monthly averaged climatology.

BATS – The climatology of the residual $prePO_4$ [µM] tracer in the upper 200 m at BATS is presented in Figure 4a. Residual $prePO_4$ varies between -0.2 to 0.2 µM in the upper 200 m. Seasonal subsurface residual negative $prePO_4$ anomalies at ~80 to 160 m depth are observed in all years from 1993 to 2016 with the exception of 2015. Seasonal pulses of residual positive $prePO_4$ anomalies (~0 – 0.1 µM) are observed immediately above the 25.8 neutral density horizon within the euphotic zone, 0 to ~80 m.

The monthly averaged climatology of residual $prePO_4$ [µM] at BATS for all data in years 1993 – 2016 is presented in Figure 4b. The subsurface residual $prePO_4$ anomaly is present throughout the seasonal cycle although it is observed to grow in magnitude beginning in May continuing through the end of the calendar year into Jan/Feb, before springtime vertical overturning circulation resets the residual $prePO_4$ concentration in the upper 200 m. The residual negative $prePO_4$ feature starts shallow at a depth of ~80 m in May/Jun that deepens over the

summer months to depths of ~80 to 200 m by years' end. There also exists a layer of residual positive $prePO_4$ anomaly at 0 – ~80 m depth that develops during Apr – Nov, concomitant with the seasonally increasing residual negative $prePO_4$ anomaly at ~80 – 200 m depth in summer and autumn.

Discussion

Our analysis found DOM remineralization within the upper mesopelagic to follow non-Redfield $-O_2$:N stoichiometry at Station ALOHA (~18–19) and the BATS station (~21). However, contrary to the findings of Abell et al., (2005) working in the subtropical North Pacific, this mechanism cannot quantitatively explain the negative $preNO_3$ anomaly present in the subsurface. Instead, we find the euphotic zone to exhibit residual positive $preNO_3$ anomalies and the upper mesopelagic exhibits residual negative $preNO_3$ anomalies at Stations ALOHA and BATS. Our directly diagnosed DOM $-O_2$:N remineralization stoichiometry from observations of AOU and DON is significantly lower than that inferred by Abell et al. (2005) (~23–30) diagnosed from AOU vs. DOC remineralization stoichiometry and likely explains this discrepancy. Thus, the fraction of AOU attributable to DOM remineralization and its AOU vs. DON stoichiometry needs to be accounted for in any study that utilizes the $preNO_3$ tracer. The traditional $preNO_3$ tracer calculation should be abandoned and replaced with the residual $preNO_3$ tracer formulation as defined in our study (Eq. 1).

We now undertake a quantitative examination of the potential contributing mechanisms to explain the subsurface rNPN anomalies and euphotic zone rPPN anomalies.

Physical mechanisms

Both the ALOHA and BATS station climatologies of the residual preNO$_3$ tracer exhibit annual cycles of rPPN anomaly formation in the euphotic zone and subsurface rNPN anomaly formation beginning at ~100 m (ALOHA) or ~80 m (BATS) that intensifies from early summer through to mid-autumn (Fig. 1 and 2). This timeframe coincides with the period of thermal stratification of the water column at the BATS station, separating the surface mixed layer, ~0 – 30 m, from the deep chlorophyll max (DCM) present at ~100 – 120 m (Navarro and Ruiz, 2013). Station ALOHA exhibits year-round stratification with the deep chlorophyll max present at ~125 m (Navarro and Ruiz, 2013). The largest rPPN anomalies are observed in the vertical zone between the surface mixed layer and the DCM at both sites, at a depth of ~50 – 100 m at station ALOHA and a depth of ~40 – 80 m at the BATS station. This vertical zone of rPPN anomaly formation coincides with the observed subsurface O_2 maximum (SOM) that has historically been a conundrum to biogeochemical explanation given the *in situ* ^{14}C-diagnosed net primary production estimates (e.g. Jenkins and Goldman, 1985; Shulenberger and Reid, 1981; Platt et al., 1989). Our rPPN volumetric rates of formation converted to O_2 units using the values in Table 1 are approximately 20 – 37% (at Station ALOHA) of the estimated SOM formation rate in the subtropical central North Pacific and ~34 – 41% (at the BATS station) of the estimated SOM formation rate in the Sargasso Sea (Shulenberger and Reid, 1981).

Subsurface rNPN anomalies begin to appear at a depth of ~100 m at station ALOHA and ~80 m at the BATS station continuing down to depths of ~200 m and ~160 m, respectively. We estimated the depth of the top of the nitracline by defining this as the depth where [NO_3^- + NO_2^-] = 0.5 µM in the monthly averaged climatologies. At Station ALOHA, the top of the nitracline varies between 120 – 130 m depth with a mean of ~126 m over the annual cycle. At the BATS station, the top of the nitracline varies between 90 – 120 m depth with an annual mean of ~102

m. Thus, the formation of rNPN anomalies is concurrent with the depth in the water column where nitrate begins to accumulate from remineralization processes at both sites and continues to form deeper into the nitracline.

What is the role of lateral physical mixing in creating the observed rPPN and rNPN anomalies? To address this question, we turn to the World Ocean Atlas annual O_2 and NO_3^- climatologies (Garcia et al., 2014a; 2014b) on the subsurface isopycnals present in the ~100 – 250 m depth layer at each site. We computed the residual $preNO_3$ tracer for the subtropical North Pacific using the values of f_{DOM} and r_{DOM} for Station ALOHA and for the subtropical North Atlantic using the values for the BATS station in Table 1. Examination of the residual $preNO_3$ tracer on the $\gamma^n = 26.5$ density surface (the surface approximately bisecting the 150 – 200 m layer near BATS exhibiting rPPN anomalies) reveals that the BATS station is immediately surrounded by waters with a residual $preNO_3$ value of ~1 µM (blue colors; Fig. S6). Waters with a residual $preNO_3$ content of ~2 – 3 µM are present to the southwest and to the northeast (red colors, Fig. S6). The lack of a residual $preNO_3$ gradient on the $\gamma^n = 26.5$ density surface in the immediate vicinity of the BATS station suggests the observed ~1 µM residual $preNO_3$ concentration present at ~150 – 200 m depth in Figure 2 represents a local signal with little mixing of waters with different residual $preNO_3$ content. Lateral advective mixing of the higher residual $preNO_3$ waters to the southwest and northeast of the BATS station would increase the residual $preNO_3$ on γ^n = 26.5 to values greater than 1 µM at the BATS station, which is not observed. Plots of residual $preNO_3$ versus the CFC-11 and CFC-12 age on $\gamma^n = 26.5$ in the North Atlantic reveal essentially no increasing or decreasing residual $preNO_3$ age gradient (Fig. S6). In summation, this evidence suggests the BATS station sits within the NW corner of a large region of the subtropical North

435 Atlantic characterized by a residual preNO$_3$ content of ~1 µM on γ^n = 26.5 that is generated
436 within the basin.

437 On the γ^n = 26.0 isopycnal which bisects the layer exhibiting the rNPN anomaly at the
438 BATS station, the site sits surrounded by waters with a residual preNO$_3$ content of ~0 µM in the
439 annual climatology, with more distant waters exhibiting rNPN anomalies south of ~27 ºN and
440 waters with rPPN anomalies north of ~37 ºN (Fig. S7). Plots of residual preNO$_3$ versus CFC-11
441 and CFC-12 age on γ^n = 26.0 again reveal essentially no residual preNO$_3$ gradient with
442 increasing age (Fig. S7). Given the lack of a residual preNO$_3$ tracer gradient with water mass age
443 and the observation of a repeating seasonal pattern of rNPN anomaly formation at the BATS
444 station on γ^n = 26.0 (Fig. 2), we conclude that lateral advective mixing cannot explain the
445 observed seasonal rNPN anomalies, instead suggestive of biological mechanisms supporting
446 rNPN anomaly formation at the BATS station.

447 Examination of the residual preNO$_3$ tracer on the γ^n = 25.4 density surface (the surface
448 approximately bisecting the 200 – 250 m layer near ALOHA) in the North Pacific within the
449 World Ocean Atlas climatology reveals that Station ALOHA sits near the southern boundary of
450 waters with a residual preNO$_3$ content of 0 – 1.5 µM that extends as far north as 40 ºN and as far
451 east as 130 ºW (Fig. S8). Waters with higher residual preNO$_3$ content of 2 – 4 µM are located to
452 the south of Station ALOHA, beginning around the vicinity of the big island of Hawaii (Fig. S8).
453 Examination of plots of residual preNO$_3$ versus CFC-11 and CFC-12 age on γ^n = 25.4 in the
454 North Pacific reveals that Station ALOHA lies between younger, low residual preNO$_3$ content
455 waters to the north with older, higher residual preNO$_3$ content waters to the south (Fig. S8).
456 Mixing of these waters along γ^n = 25.4 may explain the observed ~1 µM residual preNO$_3$

concentration present at 200 – 250 m depth in Figure 1. This feature is noticeably absent at BATS, (Figure S6) consistent with a minor role for advective mixing there.

On the $\gamma^n = 24.7$ isopycnal which bisects the density layer exhibiting the rNPN anomaly at Station ALOHA, the site is surrounded by waters with rNPN anomalies on the order of –1 – 0 µM (Fig. S9). Plots of residual $preNO_3$ versus CFC-11 and CFC-12 age on $\gamma^n = 24.7$ reveal essentially no residual $preNO_3$ age gradient (Fig. S9). Similar to the BATS station, given the lack of a residual $preNO_3$ age gradient on $\gamma^n = 24.7$ and the observation of seasonal formation of rNPN anomalies, we conclude that lateral advective mixing cannot explain the observed rNPN anomalies, suggestive of biological mechanisms.

Biological mechanisms

Lateral mixing may explain the observed rPPN anomaly below ~200 m at Station ALOHA: however, the euphotic zone rPPN anomalies and subsurface rNPN anomalies at each site are generated by a local biological mechanism. Biological formation of rNPN anomalies requires either O_2 consumption without concomitant stoichiometric nitrate accumulation or nitrate drawdown without concomitant stoichiometric O_2 production. Formation of rPPN anomalies requires either O_2 production without concomitant stoichiometric nitrate drawdown or nitrate accumulation without concomitant stoichiometric O_2 consumption. Having accounted for the non-Redfield $-O_2$:N DOM remineralization stoichiometry at each site (see Table 2 for the rate of NPN/PPN anomaly formation attributable to N-poor DOM remineralization), we hypothesize three other biological mechanisms to explain the observed seasonal formation rates and integrated quantities of concurrent rPPN accumulation in the euphotic zone and rNPN accumulation in the subsurface at the ALOHA and BATS stations: 1) biological production, export, and remineralization of N-deficient transparent exopolymer particles (TEP); 2)

heterotrophic bacterial uptake of nitrate to remineralize N-poor organic matter; 3) vertical migration of autotrophic phytoplankton down to the nutricline to acquire nitrate with subsequent photosynthetic oxygen production within the euphotic zone.

TEP – Transparent exopolymer particles (TEP) are the polysaccharide-rich exudate of phytoplankton that accumulate in the size range <1 to >100 µm in aquatic systems (Mari et al., 2017). TEP is both sticky and positively buoyant in seawater (Azetsu-Scotte and Passow, 2004), leading to aggregation and flotation towards the surface, with large enrichments of TEP present in the sea surface microlayer (Wurl et al., 2009). Being comprised of nearly pure saccharide material, TEP is a carbon rich and essentially N-deficient pool of non-sinking particulate organic carbon formed within the euphotic zone of marine systems by phytoplankton production (Alldredge et al., 1993). TEP production has been hypothesized to contribute to "carbon overconsumption" in low nutrient oligotrophic marine ecosystems (Toggweiler, 1993) where organic matter is produced in non-Redfield, C-rich/N-poor proportions. Due to its positive buoyancy (Mari et al., 2017), TEP has been viewed as a non-contributor to upper ocean carbon export; however, some portion of the TEP pool is associated with sufficient ballasting particles (e.g. clays, biogenic minerals) to achieve negative buoyancy, and may comprise a slowly sinking (a few meters per year) pool of organic carbon exported below the euphotic zone (Mari et al., 2017). TEP production and remineralization stoichiometry has the correct sense; O_2 production without Redfieldian nitrate drawdown within the euphotic zone, O_2 consumption without Redfieldian nitrate accumulation within the mesopelagic, to contribute to both the observed rPPN anomalies within the euphotic zone and rNPN anomalies in the upper mesopelagic at the ALOHA and BATS stations in our analysis.

We use field data of TEP concentrations near the BATS and ALOHA stations and a few simplifying assumptions to test for the importance of this process as a contributor to the dual rNPN/rPPN anomalies. Our estimates of the potential for TEP cycling to contribute to the observed euphotic zone rPPN and subsurface rNPN anomaly formation rates assume 1) that TEP is pure carbohydrate (CH_2O); without any N content, such that TEP production/remineralization C:O_2 stoichiometry can be assumed 1:1 (e.g. $CO_2 + H_2O \Leftrightarrow CH_2O + O_2$), and 2) that there exists a sufficiently large and dense TEP pool to sink rapidly enough to contribute to annual carbon export and O_2 remineralization budgets. Both assumptions, if incorrect, will overestimate the TEP contribution. In conjunction with TEP cycling, Coomassie stainable particles are transparent protein-containing particles (Long and Azam, 1996) that can reach similar concentrations within the oligotrophic euphotic zone as TEP (Cisternas-Novoa et al., 2015). Thus, the assumption that transparent exopolymer particle cycling delivers only C to the subsurface to drive rNPN anomaly formation may not be entirely valid. In addition, Mari et al. (2017) note that elevated TEP concentrations likely enhance material retention in the euphotic zone. Thus, our calculations that follow tend to maximize the contribution of TEP.

Cisternas-Novoa et al. (2015) measured TEP concentration depth profiles in the Sargasso Sea northeast of Bermuda on five separate occasions from February 2012 to June 2013. The profiles show a ~10 µg XG eq L^{-1} (xanthum gum equivalent) concentration excess between the upper 100 m and the 100-200 m layer (Fig. 15 in Cisternas-Novoa et al., 2015). We take this upper 100 m excess to represent the fraction of the euphotic zone TEP pool that is exported annually to the upper mesopelagic 100-200 m depth layer by a combination of physical sinking of a fraction of the TEP pool that becomes negatively buoyant or is delivered to the subsurface with wintertime vertical mixing. This assumption is supported by the observation that the

525 euphotic zone to mesopelagic TEP concentration gradient is nearly erased in the winter profile,
526 presumably due to wintertime convective mixing, and reappears following the spring bloom,
527 remaining relatively unchanged throughout the late spring/summer month profiles. TEP in
528 xanthum gum equivalents can be converted to µg C L^{-1} units using a 0.63 conversion factor
529 (Engel, 2004) and again into µM units, yielding a Sargasso Sea upper ocean concentration excess
530 of ~0.5 µM TEP-C. Integrating over the surface to 80 m depth layer (the depth where rPPN
531 anomalies switch to rNPN anomalies), we obtain a potential TEP production and export flux of
532 42 mmol TEP-C m^{-2} yr^{-1} from the euphotic zone into the upper mesopelagic. Assuming 1:1 C:O_2
533 TEP production/remineralization stoichiometry, an O_2 production flux in the absence of nitrate
534 drawdown of 42 mmol O_2 m^{-2} yr^{-1} can be ascribed to TEP production within the euphotic zone,
535 and the same flux can be ascribed to O_2 consumption without concomitant nitrate accumulation
536 from TEP remineralization in the mesopelagic. We can convert this O_2 flux to a residual preNO_3
537 equivalent using Equation 1 and the values in Table 1, yielding estimates of 3.2 – 4.5 mmol N m^{-2}
538 yr^{-1} residual preNO_3 anomaly formation rate equivalents, depending on the choice of r_{POM}.
539 Thus, TEP formation within the euphotic zone of the Sargasso Sea has the potential to explain
540 5.2 – 5.4% of the estimated rPPN anomaly formation rate and 5.1 – 7.0% of the estimated rNPN
541 anomaly formation rate within the γ^n = 25.8 – 26.3 layer (Table 2).

542 The potential contribution of TEP cycling to rPPN/rNPN anomaly formation near the
543 BATS station can be also be estimated using published sinking rates for negatively buoyant TEP.
544 Again, using the TEP profiles from the Sargasso Sea from Cisternas-Novoa et al. (2015), we
545 estimate a concentration difference of ~5 µg XG eq L^{-1} between 100 m and 200 m depth (the
546 approximate depths exhibiting rNPN anomalies). Converting to molar carbon concentration
547 yields a quantity of ~0.26 µM TEP-C that is apparently remineralized within the rNPN anomaly

548 layer. We apply the TEP sinking rate of 0.04 d^{-1} from Hamanaka et al. (2002) to estimate the rate
549 of delivery of exported TEP from the euphotic zone into the upper mesopelagic, yielding a TEP
550 supply and remineralization flux of 10 µmol C m^{-3} d^{-1}. Depth and time integrated to 15 meters
551 and one year, i.e. the depth slowly sinking TEP will sink after one year, this flux becomes 56.9
552 mmol C m^{-2} yr^{-1} or O_2 units assuming 1:1 C:O_2 stoichiometry for TEP. Conversion of this O_2
553 flux into residual $preNO_3$ equivalents yields an estimated 4.3 – 6.0 mmol N m^{-2} yr^{-1} of the
554 observed rPPN/rNPN anomaly formation rate attributable to TEP cycling. Thus, computed using
555 the sinking rate, TEP formation within the euphotic zone has the potential to explain 7.0 – 7.3%
556 of the estimated rPPN anomaly formation rate and 6.9 – 9.3% of the estimated rNPN anomaly
557 formation rate within the γ^n = 25.8 – 26.3 layer.

558 Seasonal depth profiles of TEP concentration are unavailable for the subtropical North
559 Pacific near Station ALOHA. Wurl et al. (2011) measured TEP concentration profiles south of
560 the island of Hawaii during August/September 2009. We use the upper ocean concentration
561 excess present in these profiles with the TEP sinking rate of 0.04 d^{-1} to estimate the TEP cycling
562 contribution to rPPN/rNPN anomaly formation rates near Station ALOHA. The 100 to 200 m
563 concentration excess in TEP-C is ~1 µM yielding an export and supply flux of 40 µmol C m^{-3} d^{-1}. Depth and time integrating for 15 m and one year, this flux becomes 220 mmol C m^{-2} yr^{-1}
565 (mmol O_2 m^{-2} yr^{-1}). Conversion of this O_2 flux to residual $preNO_3$ equivalents using equation 1
566 and values in Table 1, yields an estimated 16.2 – 21.8 mmol N m^{-2} yr^{-1} of the observed
567 rPPN/rNPN anomaly formation rate potentially attributable to TEP cycling at Station ALOHA.
568 Thus, TEP formation within the euphotic zone has the potential to explain 35.6 – 37.2% of the
569 estimated rPPN anomaly formation rate and 47.0 – 51.3% of the total estimated rNPN anomaly
570 formation rate within the combined γ^n = 24.2 – 25.2 layer (Table 2).

Bacterial nitrate uptake – Multiple studies have shown the uptake of nitrate and/or phosphate by heterotrophic bacteria during the remineralization of organic matter or that inorganic nutrients can limit bacterial OM consumption (e.g. Zweifel et al., 1993; Kirchman, 1994; Cotner et al., 1997; Rivkin and Anderson, 1997; Caron et al., 2000; Letscher et al., 2015). Bacterial nitrate uptake to remineralize OM has the effect of creating an NPN anomaly (O_2 consumption without concomitant nitrate accumulation) and thus can only contribute to the observed subsurface rNPN anomaly formation. It cannot contribute to either the formation of the euphotic zone rPPN anomaly or surface mixed layer drawdown of DIC. If TEP cycling is an important contributor to oligotrophic ocean C export and shallow subsurface O_2 consumption, heterotrophic bacterial nitrate and/or phosphate uptake is a likely complementary biological process, since the nutrient deficient content of TEP could require exogenous uptake of N and P from the seawater media for bacterial production when growing on TEP organic matter. This would result in an imbalance between rPPN and rNPN, in contrast to the results presented earlier.

To assess the potential contribution of bacterial nitrate uptake to our observed rNPN anomaly formation rates at the ALOHA and BATS stations, we examined the literature for estimates of bacterial C production rates and bacterial biomass C:N ratios for the Sargasso Sea and subtropical North Pacific. Carlson et al. (1996) measured bacterial production rates at the BATS station using the ^{3}H-thymidine and ^{3}H-leucine uptake methods with average euphotic zone rates of 23 pmol C L^{-1} d^{-1} by ^{3}H-thymidine and 0.41 nmol C L^{-1} d^{-1} by ^{3}H-leucine. Using a bacterial biomass C:N of 5:1 for this region (Gunderson et al. 2002) and integrating for one year and over the ~80 – 160 m thick layer exhibiting rNPN anomaly, yields an estimate of 0.17 – 3.0 mmol N m^{-2} yr^{-1} bacterial N demand. If we assume that bacteria satisfy *all* of their N demand via

uptake of seawater nitrate in this shallow subsurface layer, bacterial nitrate uptake can explain at most 0.5 – 3.5% of the estimated rNPN anomaly formation rate at the BATS station in the γ^n = 25.8 – 26.3 layer. This proposed mechanism still requires a process that removes bacterial N from the γ^n = 25.8 – 26.3 layer such that a rNPN anomaly is observed due to NO_3 uptake in the absence of stoichiometric O_2 accumulation. Diel vertically migrating grazers are a candidate mechanism whereby grazing on bacterial biomass and its eventual remineralization to NO_3 is spatially separated from respiration and O_2 consumption.

We can make a similar calculation for Station ALOHA using published ^{3}H-leucine bacterial production rate measurements (Church et al., 2004). The mean bacterial C production rate at 100 m is ~0.46 nmol C L^{-1} d^{-1}. Using the same bacterial biomass C:N of 5:1 and integrating for one year over the ~100 – 200 m thick layer exhibiting rNPN anomaly, yields an estimated 3.4 mmol N m^{-2} yr^{-1} bacterial N demand. If we again assume that bacteria satisfy *all* of their N demand from nitrate uptake, this process can explain at most 0 – 7% of the estimated rNPN anomaly formation rate at Station ALOHA in the combined γ^n = 24.2 – 25.2 layer.

Vertically migrating phytoplankton – From our analyses of the available published data, neither remineralization of N-poor DOM, TEP cycling, or heterotrophic bacterial nitrate uptake can quantitatively explain both the seasonal rPPN anomaly formation within the euphotic zone and subsurface rNPN anomaly formation observed at the ALOHA and BATS stations even with the generous assumptions made. Lastly, we examine the vertical migration of phytoplankton down to the nitracline as a potential biological mechanism to explain the dual rPPN/rNPN anomalies. The unique attributes of and evidence for vertical migration are briefly discussed here for background, as well as documentation of their presence in both oceans at or near the time-series stations. As a rare, giant component of the flora, net collections and *in-situ* observations by

divers constitute the bulk of observations, hence are somewhat out of the mainstream of current phytoplankton observations.

Flagellate motility and cyanobacteria buoyancy control has been recognized for decades as a strategy to exploit spatially disjunct light and nutrient fields (Cullen, 1985; Eppley et al., 1968, Ganf and Oliver, 1982; Hasle, 1950; Steemann Nielsen, 1939) and was suggested for non-flagellated marine species in *Pyrocystis* (Sukhanova and Rudyakov, 1973; Ballek and Swift, 1986; Rivkin et al., 1984). *Rhizosolenia* mats (macroscopic, multi-species (up to 7) associations of *Rhizosolenia* spp.; Villareal and Carpenter, 1989) have been the model for understanding this process (Villareal et al., 2014), with migration inferred for the diatoms *Ethmodiscus* spp. and large *Rhizosolenia* spp., as well as the phycomate prasinophyte *Halosphaera* spp. in addition to *Pyrocystis*. There is consistent evidence of high $\delta^{15}N$ composition of *Rhizosolenia* biomass similar to sub-nutricline N (Villareal et al., 1993, Villareal et al., 2014), internal millimolar nitrate pools that can only be acquired by direct uptake at µM concentrations (Villareal and Lipschultz, 1995; Villareal et al., 1996; Woods and Villareal, 2008), buoyancy reversals linked to nutrient status (Richardson et al., 1996), nitrate reductase activity (Joseph et al., 1997) induced only when nitrate is the primary N source, ascent/descent rates of multiple m hr^{-1} (Villareal et al., 2014; Moore and Villareal 1996), observation of *Rhizosolenia* mats from the surface to 305 m (Pilskaln et al., 2005), and compositional difference in floating and sinking mats that mirror physiological changes associated with nutrient depletion and carbohydrate ballasting (Villareal et al., 1996). A key attribute in all giant phytoplankton migrators is the multiple m hr^{-1} ascent/descent rates their large size (10^{7+} μm^3) permits (Moore and Villareal 1986). This allows the required 50–100 m vertical excursions and when coupled with the large vacuole of these giant phytoplankton, allow the necessary storage (mM concentrations in vacuoles that are 90+%

640 of total cell volume) for a multiple day migration and division cycle. Unlike the more widely
641 known zooplankton vertical migration, open ocean phytoplankton migration is a multi-day cycle
642 (Richardson et al., 1998; Villareal et al., 1996). It is asynchronous and not cued to diel rhythms
643 as in coastal dinoflagellates or vertically migrating zooplankton.
644 Giant phytoplankton are found throughout the warmer oceans of the world and are
645 specifically noted at both stations ALOHA and BATS (Figure S11-13). The required
646 characteristics of buoyancy reversals, high internal nitrate pools and rapid ascent/descent have
647 been found in multiple taxa from the Atlantic and Pacific Oceans (Villareal et al., 2014). The
648 taxa *Halosphaera* (Villareal and Lipschultz, 1995), *Ethmodiscus* (Villareal and Lipschultz,
649 1995), *Rhizosolenia* (Villareal and Lipschultz, 1995), and *Pyrocystis* (Swift et al. 1973, Rivkin et
650 al 1984, Villareal and Lipschultz 19965) occur in the Sargasso Sea and all exhibit positive
651 buoyancy and have mM internal nitrate pools. In the Sargasso Sea, the non-motile dinoflagellate
652 *Pyrocystis* has been the most extensively studied by E.J. Swift's lab in the 1980s. A 'once in a
653 generation' migration cycle (Sukhanova and Rudyakov, 1973) was proposed for *Pyrocystis*
654 based on differences in vegetative and reproductive cell maxima (~60 and 120 m, respectively).
655 Vegetative stages were positively buoyant (up to 0.2 m h^{-1}; Kahn and Swift, 1978) while
656 reproductive stages were negatively buoyant at up to 18 m h^{-1} in the Mona Passage, southwest N.
657 Atlantic (Swift et al. 1976). In the Sargasso Sea, carbon budgets (Rivkin et al., 1984) and
658 buoyancy changes upon nutrient depletion and addition (Ballek et al., 1986) all supported a
659 vertical migration life cycle. In single-cell analysis from field material collected off Bermuda,
660 *Pyrocystis* internal nitrate concentrations ranged from 0-8 mM with floating cells containing
661 significantly higher concentrations (p=0.05) than sinking cells (Villareal and Lipschultz, 1995).
662 Such elevated internal nitrate can only be acquired at µM nitrate concentrations found in the

nutricline. Abundance maxima in the upper ~200 m of the Sargasso Sea/southwest N. Atlantic range from 100-200 cells m^{-3}, with typical values reported of 18-75 cells m^{-3} (Rivkin et al., 1984), 10-50 cells m^{-3} (Ballek and Swift, 1986) and 10-30 cells m^{-3} (Swift et al., 1981). While the other migrating taxa are found in the Sargasso Sea near Bermuda, there is no data on abundance in the N. Atlantic other than for *Ethmodiscus*. *Ethmodiscus* was found at every station sampled on three cruises in the southwest N. Atlantic (n=18, ~17-25°N, 66-77°W) with abundance ranging from 0.03-4.7 cells m^{-3}. Free-living chains of *Rhizosolenia* were routinely isolated by hand-collection with SCUBA at Bermuda (Moore and Villareal, 1996a,b; Richardson et al., 1996) and were widely noted by Carpenter et al. (1977) in the Caribbean. Cleve (1900) reported *R. castracanei* (a giant, migrating diatom found both free-living and in *Rhizosolenia* mats) to occur in the Sargasso Sea as well as the tropical Atlantic, Caribbean Sea, Florida current to Newfoundland Banks, and the Azores.

In the Pacific, the range of *Ethmodiscus*, *Pyrocystis*, and *Rhizosolenia* mats includes the study site at Station ALOHA (Figures S11-13). Unlike the Atlantic where mats are generally very rare (~0.001 mats m^{-3}, Carpenter et al., 1977), *Rhizosolenia* mats dominate in the Pacific. Abundance ranges up to several hundred mats m^{-3}, depending on the mat size and enumeration methods (Villareal et al., 1996, Villareal et al., 1999; Villareal et al., 2014). Quantitative net surveys of *Ethmodiscus* north of Hawaii yielded abundance ranges of <0.1 – >2 cells m^{-3} (Villareal et al., 2007). Both *Halosphaera* and *Pyrocystis* were present, but not quantified. Further to the west, Soviet-era literature documents *Pyrocystis* at 10-50 cells m^{-3} in the upper 200 m (Sukhanova and Rudyakov, 1973; Sukahova, 1973). Free-living giant *Rhizosolenia* were observed by divers at all stations sampled in the N. Pacific (Villareal, unpubl. obs.), and overlapped 100% with *Rhizosolenia* mats (Fig. 2 in Villareal et al., 2014); *R. castracanei* was

reported across the Pacific Ocean (Fig. 8 in Semina and Levashova, 1977). It should be noted that net collections disrupt *Rhizosolenia* mats (Alldredge and Silver, 1982) and the large diameter species such as *R. castracanei* in the mats will appear as free-chains and cells in the literature.

For rNPN and rPPN development, the unique characteristics of vertical migration are that cells acquire and store nitrate at depth, transport it into the euphotic zone, and then reduce it internally to biomass concomitant with oxygenic photosynthesis. Nitrate transport calculations by vertical migration have a number of assumptions and caveats including variability in abundance, particularly for *Halosphaera* spp. (Villareal et al., 2014). However, site-specific estimates in the Pacific north of Station ALOHA yielded rates of 6–444 µmol N m^{-2} d^{-1} for *Rhizosolenia* mats. Four other taxa yielded transport rates of 3.2 (*Ethmodiscus* spp.), 9.2 (free living *Rhizosolenia* spp.), 17.0 (*Pyrocystis* spp.) and 33.2 (*Halosphaera* spp.) µmol N m^{-2} d^{-1}. These taxa exhibit basin-specific abundance patterns (i.e. *Rhizosolenia* mats are rare in the N. Atlantic; Carpenter et al., 1977, *Halosphaera viridis* has an extensive subsurface presence in the deep Mediterranean in winter (Wiebe et al., 1974); however, it is clear that the generalized rates are consistent with both the known abundance and distribution data as well as the required rNPN and rPPN rates at both the BATS station (126 – 239 and 169 – 225 µmol N m^{-2} d^{-1}, respectively) and Station ALOHA (88 – 122 and 119 – 168 µmol N m^{-2} d^{-1}, respectively). There are several implications of this. Lower abundance or turnover times of this flora will still have substantial effects on rNPN and rPPN. Patchiness in abundance (Villareal, 2007; et al., 2014) or concentration of buoyant particles by mesoscale fronts (Guidi, 2012) could lead to significant local perturbations on rNPN and rPPN.

We estimate the potential contribution of vertically migrating phytoplankton to the rNPN and rPPN anomaly features at the two stations by subtracting our estimates of the contributions of TEP cycling and bacterial nitrate uptake to rNPN and/or rPPN formation from the total observed rNPN/rPPN anomaly formation rates (presented in Table 2). By difference, phytoplankton vertical migration potentially explains 16 – 21 mmol N m^{-2} yr^{-1} or 45 – 50% of rNPN anomaly formation and 27 – 36 mmol N m^{-2} yr^{-1} or 59 – 62% of rPPN anomaly formation at Station ALOHA (Table 2). At the BATS station, phytoplankton vertical migration potentially explains 43 – 78 mmol N m^{-2} yr^{-1} or 90 – 93% of rNPN anomaly formation and 59 – 76 mmol N m^{-2} yr^{-1} or 87 – 95% of rPPN anomaly formation. These are likely underestimates because the bacterial nitrate uptake and TEP contribution are maximum estimates.

Contributions to carbon and phosphorus budgets

DIC – Vertically migrating phytoplankton can also help explain the observed summertime DIC drawdown (Gruber et al., 1998; Keeling et al., 2004) in the absence of measurable nitrate from the mixed layer at both the ALOHA and BATS stations. The concurrently operating migration cycles of different individuals would continually bring intracellular nitrate-rich migrators into the surface mixed layer where their oxygenic photosynthesis would draw down DIC and release dissolved O_2, contributing to rPPN anomaly formation within the mixed layer. High intracellular nitrate gradients within migrators (mM to nM across cell membranes) can also lead to excretion of dissolved nitrate into the water column (Singler and Villareal, 2005). Thus, nitrate leakage from migrators could help explain the observation of a presumed subsurface nitrate source supporting pico-eukaryotic phytoplankton in the mixed layer, even during the stratified summer months at the BATS station (Fawcett et al.,

2011). However, nitrogen derived from migrator-mediated nitrate excretion is required to sink out of the mixed layer in some form in order to contribute to summertime net DIC drawdown at these two sites. Regardless of how nitrate is acquired and internally reduced (by migrators or by release and uptake by non-migrating phytoplankton), it will contribute to the observed rPPN.

We can compare our estimated rates of rPPN formation within the euphotic zone with the summertime mixed layer DIC drawdown at each time-series site using assumptions on the appropriate O_2:C:N stoichiometry of production. Although seasonal rPPN formation exhibits the largest increase in $preNO_3$ concentrations at ~50 – 100 m depth, seasonal accumulation of positive residual $preNO_3$ is observed within the mixed layer (~0 – 30 m) at both sites (Fig. 1, 2).

At Station ALOHA, net community production during the six-month summer to fall period represents ~40% of the 2.3 mol C m^{-2} yr^{-1} ANCP (Keeling et al., 2004), yielding a summertime mixed layer DIC drawdown of ~920 mmol C m^{-2}. Our estimated rate of euphotic zone rPPN formation during this same seasonal period is 33 – 81 mmol N m^{-2} (Table 1). The summertime DIC drawdown can be converted to residual $preNO_3$ nitrogen equivalents using the literature range in O_2:C stoichiometries of production of 1.0 – 1.6 (Paulmier et al., 2009), and the DOM and POM weighted O_2:N stoichiometries of production (using the values in Table 1) yielding values of 7.8 – 14.3 for the C:N of summertime new production at Station ALOHA. Summertime DIC drawdown converted to $preNO_3$ equivalents is 64 – 118 mmol N m^{-2}. Thus, rPPN formation within the euphotic zone can potentially explain 28 – >100% of the mixed layer DIC drawdown at Station ALOHA.

The estimated rate of euphotic zone rPPN formation during summer-to-fall at the BATS station is 50 – 96 mmol N m^{-2} (Table 1). Net community production during this seasonal period is ~45% of the 2.3 mol C m^{-2} yr^{-1} ANCP (Gruber et al., 1998), yielding a summertime mixed

layer DIC drawdown of ~1035 mmol C m^{-2}. Conversion of the summertime DIC drawdown to $preNO_3$ nitrogen equivalents following a similar approach as our calculation at Station ALOHA uses a DOM and POM weighted C:N of 7.9 – 14.8 for summertime new production at the BATS station, yielding 70 – 131 mmol N m^{-2}. Thus, rPPN formation within the euphotic zone can potentially explain 38 – >100% of the mixed layer DIC drawdown at the BATS station.

$prePO_4$ – We also investigated for the presence of subsurface residual negative $prePO_4$ anomalies at the ALOHA and BATS stations. Station ALOHA does not exhibit a subsurface residual negative $prePO_4$ anomaly (Fig. 3), with the exception of a small anomaly present in years 2002 – 2004. There does exist a subsurface residual negative $prePO_4$ anomaly and euphotic zone residual positive $prePO_4$ anomaly at the BATS station (Fig. 4), present throughout the time series and monthly averaged climatology that is coincident in both seasonal timing and depth/density layer location as the rNPN and rPPN anomalies (Fig. 2). Carbon to phosphorus ratios exhibit their global maxima in the subtropical North Atlantic for phytoplankton biomass (Martiny et al., 2013), dissolved organic matter (Letscher and Moore, 2015), and exported organic matter (Teng et al., 2014). The hypothesized phosphorus limitation of this basin (Ammerman et al., 2003; Moore et al., 2004) may explain the contrasting observations of the presence of a residual negative $prePO_4$ anomaly at the BATS station in the North Atlantic while not at Station ALOHA in the North Pacific. Because of the many observations of elevated C:P across organic matter pools in the North Atlantic, we tested for the theoretical value of $R_{-O2:P}$, the stoichiometric ratio of O_2 consumed to phosphate released during the remineralization of organic matter, needed to eliminate the subsurface residual negative $prePO_4$ anomaly at the BATS station. This theoretical value of $R_{-O2:P}$ was found to be ~1000:1 (Fig. S10), which is ~4x higher

776 than the inferred $R_{-O2:P}$ for the North Atlantic from an inversion of subsurface O_2 and phosphate
777 data (DeVries and Deutsch, 2014).

778 We hypothesize that P-limited or P-stressed vertically migrating phytoplankton also take
779 up phosphate at the nutricline in combination with nitrate to contribute to both the observed
780 rNPN/rPPN and the subsurface residual negative $prePO_4$ anomaly present at the BATS station.
781 Limited sampling in the waters between Hawaii and California indicated N:P ratios were not
782 significantly different between sinking and ascending *Rhizosolenia* mats (N:P ~26-30) while C:P
783 ratios were significantly different (p = 0.05, C:P sinkers = 388 ± 66; C:P ascending = 221 ± 43).
784 This is consistent with simultaneous uptake of N and P at depth, but carbon consumption at
785 depth relative to the surface. Further data on phosphate composition of vertically migrating
786 phytoplankton are needed to confirm our hypothesis.

787

788 **Concluding Remarks**

789 Subsurface residual $preNO_3$ anomalies cover a large portion of the subtropical ocean
790 (Fig. 5). Our analyses have confirmed and emphasized that the Abell et al. (2005) use of non-
791 Redfield DOM stoichiometry in the calculation of $preNO_3$ is required, and an explicit derivation
792 of r_{DOM} is needed. The residual $preNO_3$ calculation revealed a subsurface rNPN anomaly that is
793 not accounted for by organic material remineralization. Our consideration of three possible
794 contributing biological mechanisms suggest that the dominant role (in decreasing order of
795 importance) is played by vertically migrating giant phytoplankton, TEP
796 formation/remineralization, and bacterial utilization of nitrate (Table 2). The analyses also
797 revealed a near-surface rPPN anomaly that is approximately balanced and concurrent with the
798 rNPN anomaly. This feature is coherent with the subsurface oxygen maximum (SOM) and we

interpret this as evidence that the "missing" nitrate from the rNPN anomaly is mechanistically linked to the SOM. The seasonal euphotic zone rPPN anomaly can also explain a significant fraction of the unexplained summertime drawdown of DIC from the mixed layer at both sites. Whether this phenomenon is predominately carried out by TEP production and export, vertically migrating phytoplankton, or a combination of both awaits future direct field observations.

Fraga (2001) developed an independent assessment of the impact of vertical migration on the NO tracer (functionally related to our residual preNO$_3$ tracer) based on first principles of photosynthetic production and biosynthesis of biomass. For ecosystems containing both coastal dinoflagellates and oceanic diatoms, a subsurface minimum in NO and a related tracer, NCO (NO corrected for the stoichiometry of carbohydrate synthesis) formed. For migrating *Rhizosolenia*, the NO and NCO minimum was at ~150 m with negative anomalies from ~80 to ~200 m (Fig. 6 in Fraga, 2001). The Fraga (2001) formulation also included an explicit term for release of soluble carbohydrate (functionally equivalent to TEP). Migrating phytoplankton can clearly provide a mechanistic linkage via upward nutrient transport to the observed NO anomalies.

More observations of upper ocean, surface to ~200 m, abundance estimates of the vertically migrating phytoplankton taxa, their intracellular nitrate and phosphate contents, and their migration timescales are needed to confirm the hypothesis by multiple authors (e.g. Cullen, 1985; Richardson et al., 1998; Fraga, 2001; Villareal et al., 2014) of this flora's important role in nutrient transport and rNPN/rPPN anomaly formation at the time-series stations (this study). Given the circumglobal, warm-water range of this oligotrophic flora (Fig. S11-S13), it is reasonable to expect upward nutrient transport throughout the subtropical gyres. TEP may contribute as well, depending on the stoichiometry of production/remineralization and shifts in

buoyancy characteristics. More information on the mass quantities of the positively and negatively buoyant TEP within the euphotic zone and its C:N content is needed to better constrain the role of this mechanism in rPPN/rNPN anomaly formation in the subtropics. In addition, *Rhizosolenia* mats are embedded in a TEP matrix (Pilskaln et al., 2005), so it is likely that all three biological mechanisms we investigated are non-mutually exclusive with vertically migrating phytoplankton contributing to TEP production/export, nitrate transport across the nitracline into the euphotic zone, and bacterial nitrate uptake to remineralize N-deficient TEP. While phytoplankton TEP production appears to be favored in the upper water column, positively buoyant TEP production/formation in the nutricline could also serve to provide a means for transporting entrained particulates upward into the euphotic zone. Both migration and TEP are difficult to measure and the challenge will be to develop methods and time-series to record these biologically driven processes at the requisite time and space scales.

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Table 1. Residual negative preNO$_3$ (rNPN) and residual positive preNO$_3$ (rPPN) anomaly formation rates at stations ALOHA and BATS.

	Depth (m) or Neutral Density γ^n		f_{DOM}	r_{DOM}	r_{POM}	rNPN		rPPN	
						μmol N m^{-3} d^{-1}	mmol N m^{-2} yr^{-1}	μmol N m^{-3} d^{-1}	mmol N m^{-2} yr^{-1}
ALOHA	0 – 100 m		0.5	18.1	10.6	--	--	2.4 ± 0.8	43.5 ± 10.5
					6.9	--	--	3.3 ± 1.1	61.2 ± 20.2
	24.2 – 24.7		0.5	18.1	10.6	3.0 ± 1.5	17.9 ± 7.4	--	--
					6.9	2.8 ± 1.4	28.3 ± 9.6	--	--
	24.7 – 25.2		0.5	18.9	10.6	2.5 ± 1.4	13.7 ± 7.8	--	--
					6.9	1.6 ± 0.8	18.1 ± 8.8	--	--
Total	r_{POM} = 10.6					--	31.6 ± 10.8	--	--
Total	r_{POM} = 6.9					--	46.4 ± 13.0	--	--
BATS	0 – 80 m		0.4	21.1	10.6	--	--	4.1 ± 0.8	61.8 ± 12.2
					6.9	--	--	5.8 ± 1.2	82.1 ± 13.8
	25.8 – 26.3		0.4	21.1	10.6	3.8 ± 3.1	46.0 ± 39.3	--	--
					6.9	5.5 ± 2.7	87.1 ± 41.0	--	--

Table 2. Contribution of N-poor DOM remineralization to NPN and PPN anomaly formation rates as well as contributions to rNPN and rPPN anomaly formation rates by presumed processes at the time-series sites. NPN/rNPN is for feature on γ^n = 24.2 – 25.2 at station ALOHA and γ^n = 25.8 – 26.3 at the BATS station. Ez PPN/rPPN is for feature at 0 – 100 m depth at station ALOHA and 0 – 80 m depth at the BATS station.

						Proposed attributable process		
Station	$preNO_3$ Feature		N-poor DOM remineralization		Residual $preNO_3$ Feature	TEP production & remineralization	Bacterial nitrate uptake	Phytoplankton vertical migration
ALOHA	NPN		1 – 16 mmol N m^{-2} yr^{-1}		rNPN	16 – 22 mmol N m^{-2} yr^{-1}	0.0 – 3.4 mmol N m^{-2} yr^{-1}	16 – 21 mmol N m^{-2} yr^{-1}
	Ez PPN		2 – 21 mmol N m^{-2} yr^{-1}		Ez rPPN	16 – 22 mmol N m^{-2} yr^{-1}	--	27 – 36 mmol N m^{-2} yr^{-1}
					% rNPN	47 – 50%	0 – 7%	45 – 50%
					% Ez rPPN	37 – 41%	--	59 – 63%
BATS	NPN		1 – 14 mmol N m^{-2} yr^{-1}		rNPN	3.2 – 6.0 mmol N m^{-2} yr^{-1}	0.2 – 3.0 mmol N m^{-2} yr^{-1}	43 – 78 mmol N m^{-2} yr^{-1}
	Ez PPN		2 – 17 mmol N m^{-2} yr^{-1}		Ez rPPN	3.2 – 6.0 mmol N m^{-2} yr^{-1}	--	59 – 76 mmol N m^{-2} yr^{-1}
					% rNPN	6 – 7%	0.5 – 3.5%	90 – 93%
					% Ez rPPN	5 – 7%	--	93 – 95%

Figure 1. (a) Climatology of the residual preNO$_3$ tracer [µM] in the upper 250 m at station ALOHA (22.75 ºN 158 ºW) for a value of r_{POM} = 10.6. Black contour lines show neutral density γ^n = 24.2, 24.7, and 25.2. (b) The monthly averaged residual preNO$_3$ [µM] climatology for all data in years 1989 – 2016.

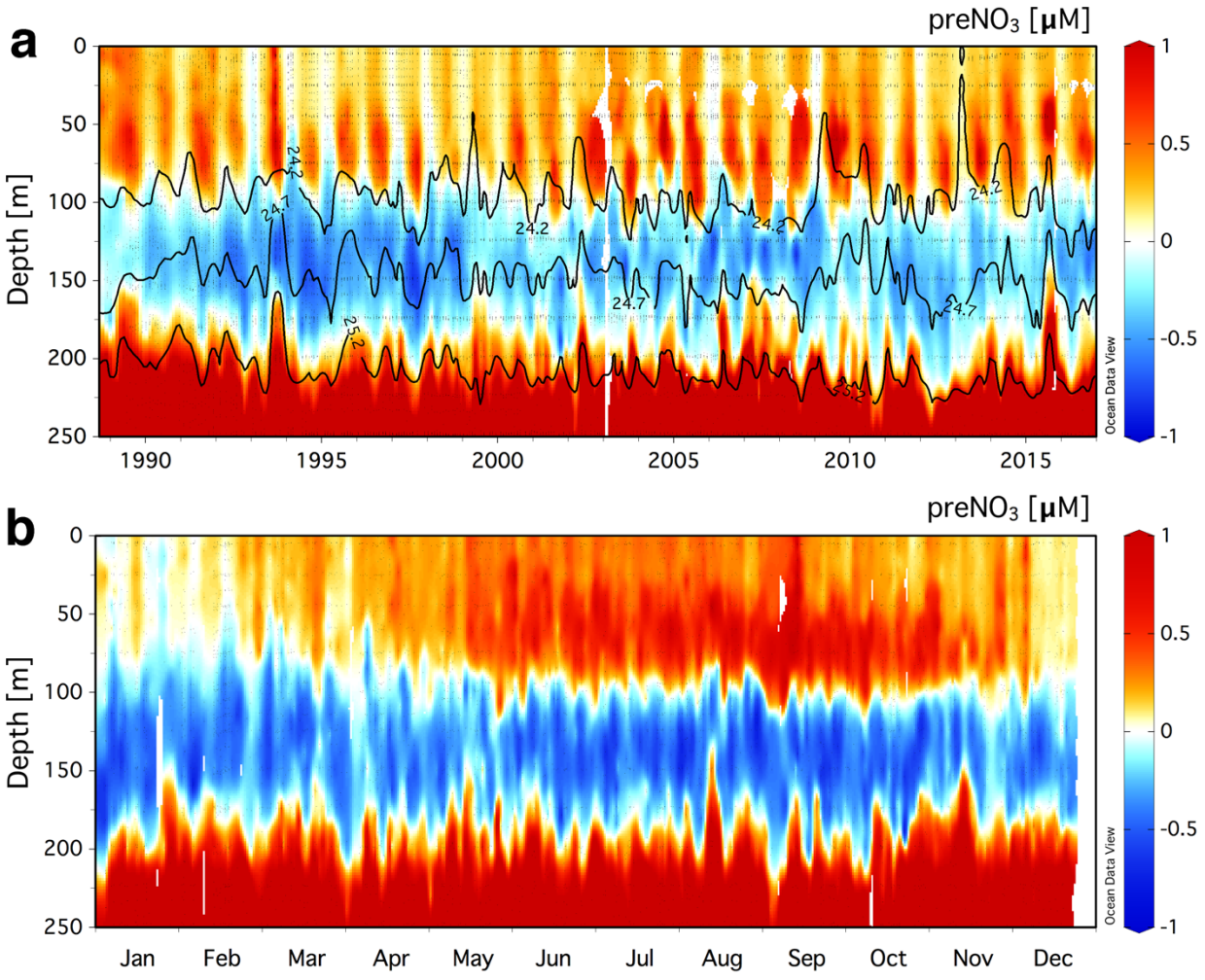

Figure 2. (a) Climatology of the residual preNO$_3$ tracer [µM] in the upper 200 m at the BATS station (31.67 ºN 64.17 ºW) for a value of r_{POM} = 10.6. Black contour lines show neutral density γ^n = 25.8 and 26.3. (b) The monthly averaged residual preNO$_3$ [µM] climatology for all data in years 1993 – 2016.

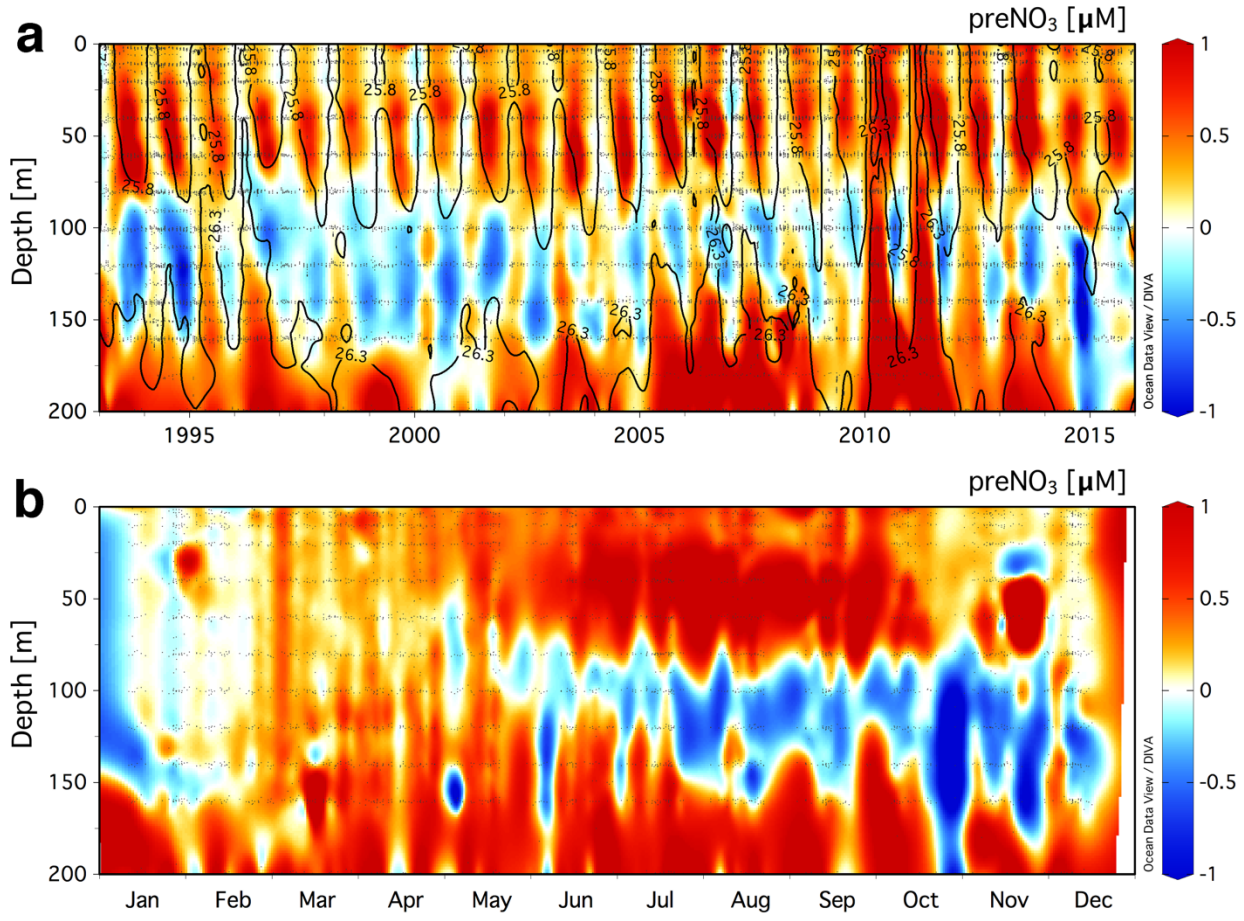

Figure 3. (a) Climatology of the residual $prePO_4$ tracer [µM] in the upper 250 m at station ALOHA (22.75 ºN 158 ºW) for a value of r_{POM} = 10.6. Black contour lines show neutral density γ^n = 24.2, 24.7, and 25.2. (b) The monthly averaged residual $prePO_4$ [µM] climatology for all data in years 1989 – 2016.

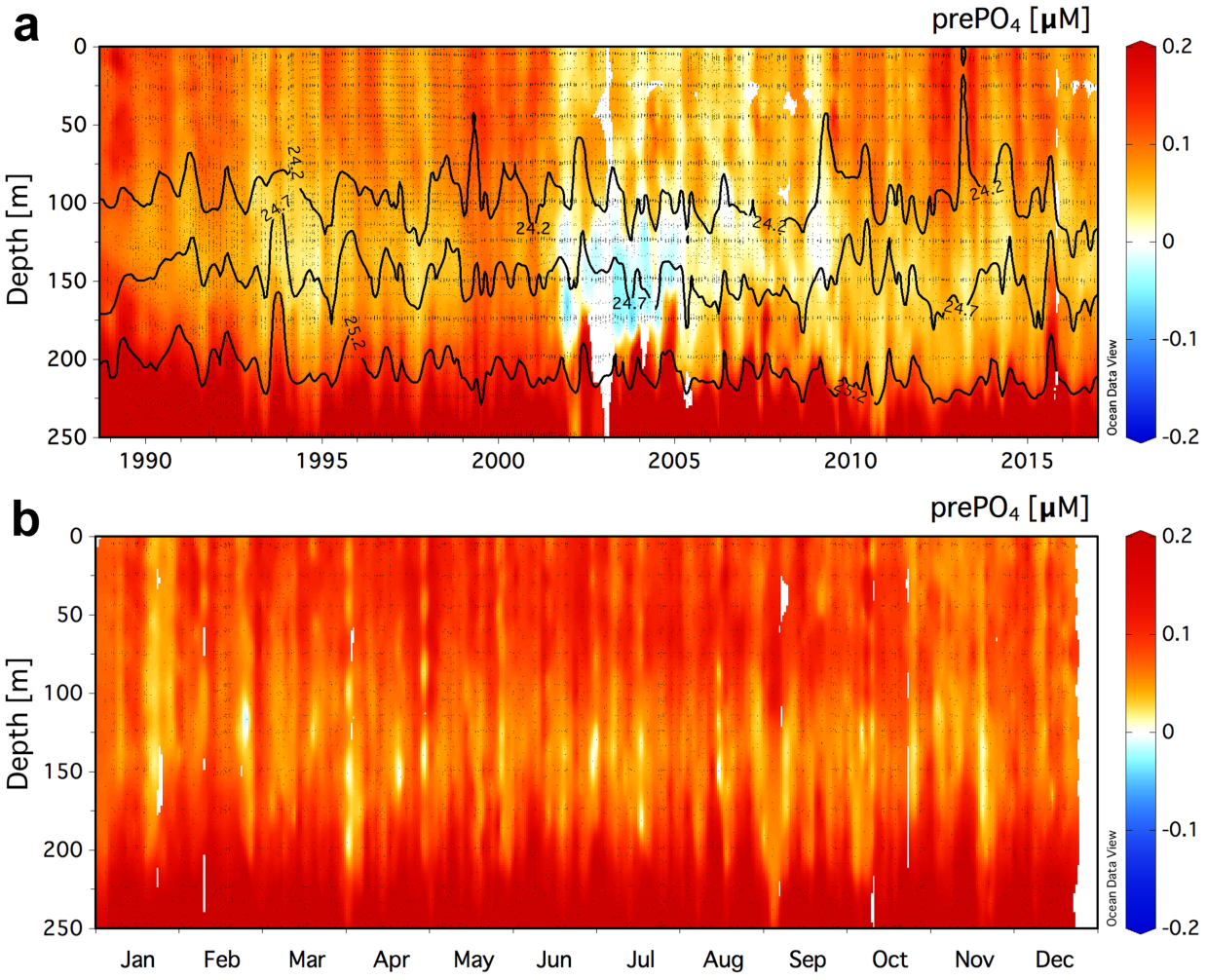

Figure 4. (a) Climatology of the residual $prePO_4$ tracer [µM] in the upper 200 m at the BATS station (31.67 ºN 64.17 ºW) for a value of r_{POM} = 10.6. Black contour lines show neutral density γ^n = 25.8 and 26.3. (b) The monthly averaged residual $prePO_4$ [µM] climatology for all data in years 1993 – 2016.

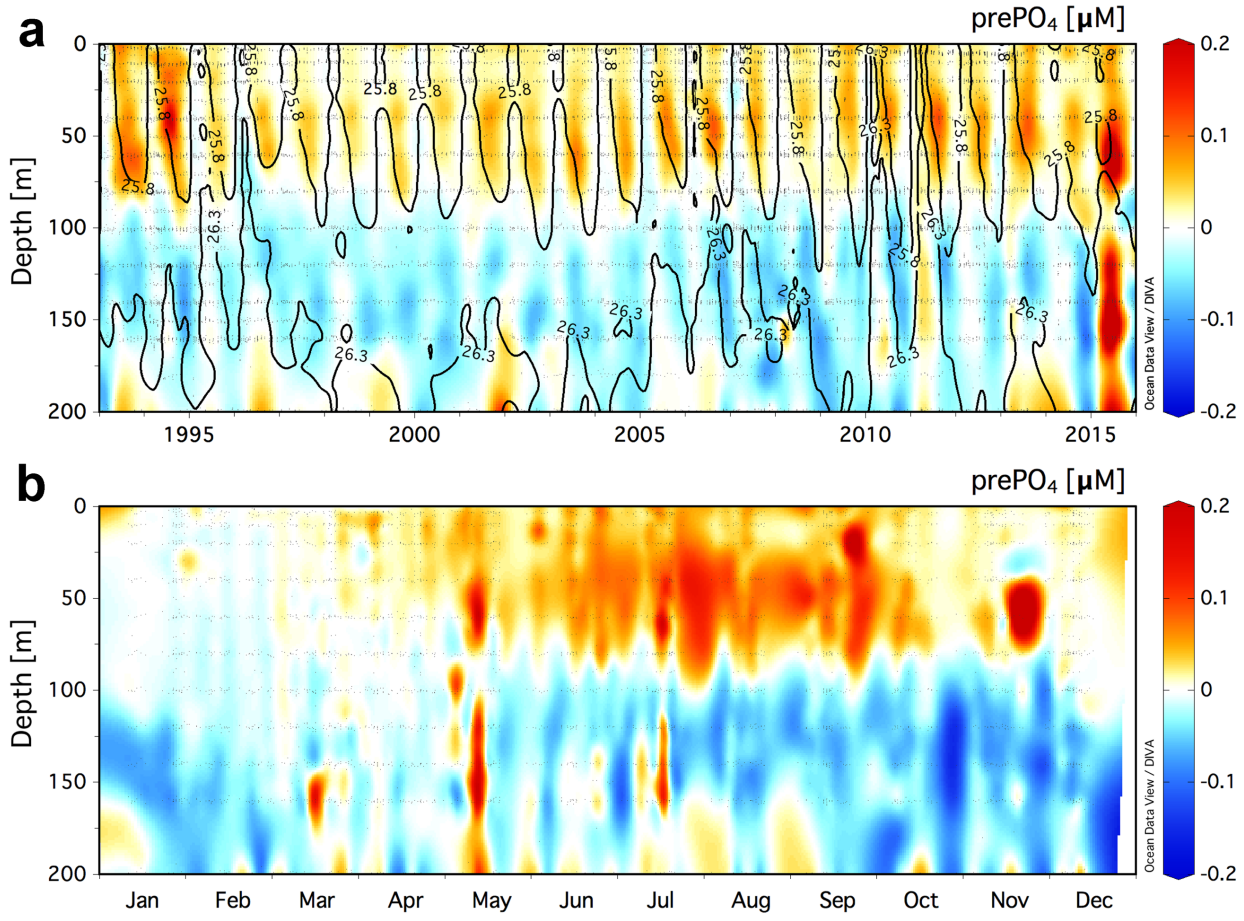

Figure 5. Seasonal climatology of the residual preNO$_3$ tracer [µM] at 150 m depth from the World Ocean Atlas, 2013, 1º climatologies of O_2 anomaly and nitrate. Residual preNO$_3$ is calculated using values of f_{DOM} = 0.5, r_{DOM} = 20.0, and r_{POM} = 8.75.