Interactive comment on “Organic nutrients and excess nitrogen in the North Atlantic subtropical gyre” by A. Landolfi et al.

Anonymous Referee #2

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General comments:

This manuscript uses new measurements of [NO3], [PO4], [TDN] and [TDP] to assess rates of the development of nonRedfieldian nutrient ratios in the subtropical North Atlantic along a zonal transect at ~24 N that may be attributable to N2 fixation. Similar to a Gruber and Sarmiento (1997) and/or Hansell et al. (2004 and 2007) approach, these authors use an isopycnal type model to track the development of N:P ratios in excess of 16:1 ratios along potential density surfaces that are paired with CFC-12 tracers to determine the rate that these gradients develop.

The use of new data, especially including organic forms of nitrogen and phosphorus,
is commendable, and the measurements presented here are valuable and will greatly extend our data set for the North Atlantic Ocean.

This reviewer's main concerns include:

1) It is not clear from the figures or data shown that there are actual gradients in any of the parameters (i.e., DINxs, TONxs, TNxs) along the isopycnals studied (see Figures 5, 8, 10, 11). This is not addressed by the authors. Either the figures are poorly designed and fail to show the gradients the authors have documented, or there are essentially no gradients in the data; the latter case would be consistent with the recent analysis of Deutsch et al., (2007) who found very low P* (a parameter related to N*) gradients in the North Atlantic; this possibility is not addressed by the authors. Moreover, the authors consistently pick maximum accumulation rates of nutrients along the isopycnals, without explaining or justifying the choice of the maximum instead of average accumulation rates. This reviewer strongly recommends that the authors use statistics to support their claim that their gradients are statistically significant; especially in the case of Figures 5, 8, 10, 11, it looks like there is no difference, just noise, between the western and eastern ends of the transect. Figure 10 could benefit from trend lines being added to show the gradients being assessed, as well as statistics for those lines.

2) The authors did not sample the initial conditions of the isopycnal surfaces being studied to characterize the preformed nutrient concentrations that are the lynch pin of this analysis. This is somewhat understandable (not every cruise allows all the sampling one wants); however, for the analysis presented here, these values are critical. The authors are consequently forced to use the data of others to constrain the preformed nutrient content of each isopycnal. How the end members for the isopycnal model were chosen, and defining the absolute values of those end members is critical, especially given the concerns highlighted immediately above. While the ratio of the nutrients is given for the preformed conditions of each isopycnal, the [NO₃], [PO₄], [TDN] and [TDP] are not. These measurements would allow readers to compare with
measurements made in other locations to evaluate this information, and should be provided.

3) Data quality, especially [TOP] measurements; there is a maximum in [TOP] at \(\sim 350\) m in the eastern side of the transect (Figure 3); this seems suspicious; values are higher at 350 m than in most parts of the surface ocean, and this feature is not addressed by the authors. Indeed, it looks like the high [PO4] in that region (Figure 2) are influencing the [TOP] values, which cannot be measured directly, but must be calculated as the difference of [TDP] and [PO4]. [TOP/TON] are notoriously difficult measurements to make, especially when [DIP/DIN] are high. Moreover, small errors in [P] measurements lead to large errors in DINxs/TONxs/TNxs calculations, since any small error in [P] is magnified by the 16 multiplier. This reviewer strongly suggests the following sensitivity test: if this [TOP] hot spot; was removed, what would the effect on TONxs and TNxs accumulation rates be? How much of the gradient (and thus rates) are driven by what could be argued, given the current lack of discussion by the authors of this feature, is an artifact? It seems that if [TOP] are high in the east and [TON] are low, but that ratio changes; to the west (which the authors claim), then an artificially high [TOP] on the eastern side of the basin would strongly bias the rates of TONxs development to be far too high. This could significantly impact the conclusions of the authors, who claim that TONxs is a main contributor to TNxs in the North Atlantic.

Review criteria:

1. Does the paper address relevant scientific questions within the scope of BG? Yes; quantifying marine N fluxes, especially from N2 fixation, using geochemical techniques is a timely and relevant topic.

2. Does the paper present novel concepts, ideas, tools, or data? Yes; the manuscript incorporates organic nutrients into calculations of excess N; in the North Atlantic; this is a relatively new approach (see Hansell et al., 2007), and the
data presented are new and valuable.

3. Are substantial conclusions reached? Yes

4. Are the scientific methods and assumptions valid and clearly outlined? The methods described in the text are very clearly presented, and the analytical methods used are valid; however, this reviewer would like to see much more detail describing the following methods and assumptions.

One addition that would be nice to have would be the station locations and depths that nutrients were sampled at on the cruise, as well as the station locations and depths that the pCFC-12 was sampled at, since these were apparently different (p. 695, lines 5-6). Also, why were interpolations between nutrients and pCFC-12 done on a constant depth grid and not constant potential density surface? Which is more appropriate?

Some other assumptions that are key to this analysis but deserve more description: End member assumptions &8211; what about error analysis/range of estimates for preformed nutrients? This is fundamental to the analysis, but minimal details are given &8211; station location? Date sampled? Especially for the &8220;preformed&8221; nutrients on each isopycnal - why are all samples below 50 m used? Why not the samples from less than 50 m, and those only? How deep does &gt; 50 m include? How many samples were analyzed for each end member? This reviewer understands that there is a very limited amount of this kind of data, but the details that the authors have should be included.

5. Are the results sufficient to support the interpretations and conclusions? See above concerns regarding the [TOP] at 350 m in Fig 3. Additionally, the apparent lack of gradients in TNxs/TONxs/DINxs need to be addressed. Simply having an &8220;excess&8221; of any of these parameters does not mean there are any significant rates of processes that generate these values occurring - their must be gradients in these parameters to be able to calculate a rate, not just a (constant) deviation from 16:1. Finally, the preformed nutrient composition needs to be more comprehensively described.
6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? More information on end member details, including station location, and concentrations of [NO3], [PO4], [DON] and [DOP], not just DINxs/TONxs/TNxs would be appreciated

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes

8. Does the title clearly reflect the contents of the paper? Yes

9. Does the abstract provide a concise and complete summary? Yes

10. Is the overall presentation well structured and clear? Yes

11. Is the language fluent and precise? Yes

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Table 1; please also list the [NO3], [PO4], [TON], [TOP], [TDN] and [TDP]. Also, why are values deeper than 50 m used? Why not shallow values? What is the mixed layer for these waters? What was the date these concentration measurements are from/what day were the samples collected? How does that correspond to when the maximum winter mixed layer depth occurs?

Table 2; please also include minimum rates of development for TNxs, TONxs and DINxs.

Table 7; units are inconsistent between title and TNxs rate column?

Figure 5; It is not clear there are any gradients in DINxs, TONxs or TNxs. Without wanting to prompt the authors to artificially enhance their figures to suit their findings, it would seem that if the authors want to calculate DIN/TON/TNxs, they first need to show that there is a gradient in at least one of these parameters in their dataset;
Figure 5 does not clearly show any such gradient in any of these fields. Perhaps the scales should be changed, but this reviewer is skeptical that significant gradients in any of these fields are actually present; Indeed, isn’t the lack of a gradient in any of these parameters consistent with the findings of Deutsch et al. (2007)?

Figure 7 & #8211; Add labels above each panel indicating which scenario (i.e., DINxs, TONxs, etc.) is shown?

Figure 8: While Figure 8 indicates variability, it is not clear to this reviewer that there is a significant difference in the rates of DINxs, TONxs or TNNxs accumulation from the eastern to the western side of the basin. The authors could break the zonal transect up into segments and do a statistical analysis to see if there are statistically significant differences between the eastern, central and western segments.

Figure 10: Add lines to & #8220;trends& #8221;, report r2, and do statistical analysis to determine whether correlations are significant.

Figure 11: Add trend lines to isopycnals that account for the largest fluxes?

14. Are the number and quality of references appropriate? Yes

15. Is the amount and quality of supplementary material appropriate? N/A

Technical comments p.686, Abstract: what are the source of the two different TN flux estimates, and what is the 2nd TN flux estimate being revised upwards from? What is the DINxs flux estimate?

p. 687, line 5: nutrient, not nutrients

p. 687, line 9: Is Hansell and Carlson, 2001, really an appropriate reference for N2 fixation fluxes to the North Atlantic, or do the authors mean Hansell et al., 2004?

p. 687, line 18: it is unclear to this reviewer that the 16:1 ratio reflects the biological demand for these nutrients; it is true that 16:1 reflects the average ratio of N:P in phytoplankton biomass; please give reference for the & #8220;demand& #8221; statement,
or consider dropping/rephrasing.

p. 687, lines 27-29: this reviewer might more carefully phrase, atmospheric deposition contributions are small; see Hansell et al., 2007.

p. 688, lines 9-10: would selective uptake of PO4 lead to positive N* anomalies? Perhaps only in surface waters, but N* is not usually applied in euphotic waters - would preferential PO4 uptake manifest as positive N* in the thermocline, once the biomass is remineralized?

p. 692, line 3: isopycnal surface 27.5 extends below 400 m, esp. on the western side of the basin;

p. 692; lines 4-5: was TON/TOP really > 16 at 350 m on the eastern side of the transect?

p. 693, lines 1, 14, and throughout: DINex should read DINxs, etc.

p. 693, line 13: Wouldn’t atmospheric deposition of any form of N and/or P, not just inorganic N, in ratios > 16:1 result in positive DINxs anomalies, since atmospheric deposition will likely be transformed to its inorganic constituents by subsurface bacteria? That is, preferential remineralization of DON relative to DOP from atmospheric sources is not required since the TN:TP of atmospheric deposition is > 16:1; Analogous question for p. 693, line 18.

p. 693: what about causes of negative TONxs and TNxs anomalies?

p. 694, line 3-4: this reviewer suggests adding TN and TP to clarify.

p. 695, lines 9-15: Given the problems in estimating TNxs on.sigma theta surfaces < 26.0, why not drop these from your calculation? How different would your results be if you dropped these values?

p. 695, lines 22-24: please see comments above on Figure 8. Also, please show the correlation between suspended PN d15N and whichever spatial pattern (TNxs?
DINxs? TONxs?) is being referred to, as well as the r2 value and whether or not that correlation is significant, and why you would expect PN d15N to be related to DINxs/TONxs/TNxs development.

p. 697/FIG. 10: shouldn’t we expect to see trends (especially increases) in TN/TON/DINxs with increasing CFC-12 age? The authors could indicate such a gradient by plotting lines through the DINxs and TONxs data in each panel. The graphs right now suggest there is no change in either DINxs or TONxs with increasing ventilation age, and thus no accumulation of TNxs in the North Atlantic.

p. 697, lines 6-9: how do the authors justify using the maximum value in Table 2 to calculate TNxs accumulation rates? Why isn’t the average value used?

p. 699, lines 17-20: what is the maximum winter mixed layer depth for 24.5 N 65 W? Is 163 m truly isolated from the surface so that it can accumulate nutrients, or is it ventilated annually? For how many years has it been isolated from the surface?

p. 699, lines 24-26: Could the authors give an example of the short time scale processes affecting TONxs on the 26.5 isopycnal? Since the 26.5 isopycnal is well below the euphotic zone, especially on the western side of the basin, for most of the year, what processes are the authors referring to?

p. 700, lines 5-12: Again, why are maximum accumulation rates used, and not mean? How is this justified?

p. 701, lines 2-3: It looks like the TN accum rates are 2x > than the DINxs accum rates, which would make the TNxs accum rate 100% greater than the DINxs accum rate; what does the 50% greater refer to?

p. 701, lines 11 onward: please specify whether you are referring to wet or dry deposition estimates; there are typically considerable differences in the magnitudes of these fluxes to the ocean.

p. 702, line 2: spelling of Prochlorococcus
p. 702, lines 13-15: Knapp et al. and Meador et al. only measured natural abundance d15N variation, not enriched samples. Also, note the data from the BATS site, as well as Hansell and Carlson, 2001, which corroborate the lack of seasonal changes in [DON] in the Sargasso Sea described by Knapp et al., 2005, and others in the N Pac.

p. 702, lines 20-25: Is the quantity of LMW DON described in Meador et al., 2007, sufficient to generate the observed trends in TNxs in the North Atlantic? Some simple calculations in the text could help address this question. This reviewer’s suspicion is no, the magnitude of that potential flux is far too small to generate the observations.

p. 702, line 25: excretion is a source of low d15N N, not enriched d15N; see Checkley and Miller, 1989. Also, it is not obvious that the mechanism described here will result in excess DON accumulation; invoking the microbial loop seems to suggest that there could be transfers between inorganic and organic pools, and without evidence for the accumulation of DON at depth, it is not clear to this reviewer that cycling through LMW DON would lead to TONxs in the subsurface.

p. 703, line 13: what is 50; referring to? What units, what estimate is being compared? Please give units and a reference. It seems like throughout the manuscript these authors are roughly doubling DINxs estimates of new N accumulation in the North Atlantic, although this sentence almost reads as if estimates are being increased 50 fold, which I suspect is not what the authors intend.

p. 703, conclusion: what biological and geochemical estimates of N2 fixation rates are the authors trying to reconcile? Specific numbers and references would be useful here.

Interactive comment on Biogeosciences Discuss., 5, 685, 2008.