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Biogeosciences Discussions

Interactive comment on "Organic nutrients as sources of N and P to the upper layers of the North Atlantic subtropical gyre along 24.5 N" *by* A. Landolfi et al.

Anonymous Referee #1

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This manuscript intends to address a relevant question in oceanography: what influences organic nutrient concentrations in the surface ocean. However, this is an open topic because there are so few methods that can give us robust information with which to evaluate this question. The authors have used a variety of methods, some perhaps more useful than others, and the stated confidence of the authors' results does not reflect the considerable uncertainty associated with the methods used. Additionally, the authors have invoked multiple assumptions that are poorly justified given how fundamental they are to the interpretation of the data.

The authors have done a significant amount of work, much of which is probably worthy

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of publication (although some of the useful data in this manuscript, i.e., the TON and TOP concentration measurements, were already published in a previous manuscript in Biogeosciences). However, the interpretation of the data, especially the underlying assumptions, should be re-evaluated and couched in more cautious language that better reflects the actual certainty of the results based on the methods used.

Major comments 1) One of the fundamental assumptions made in this manuscript is that DON and DOP are only produced in waters with >0.1 mg m-3 chl a. This assumption needs a reference, or at the very least, an explanation – this assumption underpins the whole analysis, and seems questionable, and potentially contradictory with previously published work. Since bacterial production and consumption of DOM is a fundamental aspect of the "microbial loop", and since bacterial activity is not indicated by chl a measurements (but would affect MUF-P and L-AMC uptake rates), it's not clear why the authors use this apparently arbitrary cutoff. Since regenerated production dominates in oligotrophic gyres, couldn't we expect more DON/DOP cycling (including production) in regions with a more active microbial loop/more active recycling of nutrients than say a region with higher f-ratios? Moreover, are the concentrations of DON or DOP between the "young" and "old" waters, as defined by the authors, statistically significantly different? Related to this is the "artificial age tracer" used in this analysis, where the age of surface waters is based on the time in a model since the waters supported >0.1 mg m-3 chl a. This age model is then used with the MUF-P and L-AMC uptake rates to determine DON and DOP turnover times. The combination of the assumption that DON and DOP are only produced in waters supporting >0.1 mg m-3 chl a, and then the calculation of the water mass age from the model, I would argue contribute the greatest uncertainty to this analysis, and are possibly flawed metrics. Since the manuscript's analysis rests on these metrics, I have to question how useful the reported DON and DOP turnover rates are.

2) The authors want to use the d15N of PNsusp to infer the sources of new N to surface waters. However, as the authors describe, there are multiple sources of low-d15N

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N to the N Atlantic, including 1) N2 fixation, 2) regenerated NH4, and 3) atmospheric deposition. Additionally, the authors identify multiple sources of high d15N material, including 1) subsurface NO3, and 2) organic matter from higher trophic levels. The authors only claim to have eliminated the input of high-d15N material by higher trophic levels in this study, leaving at least three sources of low-d15N N to contribute to PN-susp d15N. Additionally, the authors claim that isotopic fractionation due to incomplete consumption can be eliminated in oligotrophic waters – this may be the case for NO3, but the authors also claim that DON maybe a source of PNsusp (and vice versa), and since the authors demonstrate that DON (and PON) is not fully consumed, the isotopic fractionation during DON (PON) consumption would be relevant to their interpretation of the d15N of PNsusp in this model.

Simply put, the authors do not have enough information to determine what the sources of N are to PNsusp pool, making it a bad proxy for the sources of new N to the surface waters of their transect. This undermines the authors' categorization of four biogeochemical "zones" along the 24.5 deg N transect. To bolster their argument, they could use statistics (they may need to use statistics for non-Gaussian/non-normally distributed data) to show whether or not the d15N of the PNsusp is statistically significantly different between their zones. It looks like the data are not statistically significantly different – if the data aren't statistically different, I wonder how they can justify dividing up their transect into these zones?

3) I applaud the authors for trying to distinguish what the relative contribution of inorganic and organic nutrients are to new production. This is a relevant question, and is extremely difficult to answer – all methods have their liabilities. While using the turnover of MUF-P as a proxy for APA activity might be valid for estimating DOP use, I am more concerned about using the L-AMC substrate as a proxy for DON use. The variability of DOP functional groups is much more limited compared with DON functional groups, making MUF-P a better proxy for DOP turnover than L-AMC is for DON turnover. Since leucine, and amino acids more generally, are a minor fraction of bulk surface ocean

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DON, L-AMC isn't a good proxy for estimating turnover rates of the bulk DON pool – the turnover rates of leucine are likely much higher compared to the rest of the DON pool. Unfortunately there isn't a good model compound to use for estimating DON turnover rates using these or other methods (although see 15N tracer work of Bronk and Mulholland). I would argue that this further limits the utility of the authors' estimate of DON turnover, and the confidence in the conclusions that the group comes to regarding this should be modified appropriately. DON is enigmatic, and we know little about its turnover, or which sources or sinks dominate at any one time or place, but putting undue confidence in a compromised method does not advance the field or our understanding of DON turnover rates.

Finally, this manuscript would benefit from incorporating some recently published data:

-Sohm and Capone, 2010, Global Biogeochemical Cycles, Zonal differences in phosphorus pools, turnover and deficiency across the tropical North Atlantic Ocean -The recent special issue of Marine Chemistry, V. 120, Issues 1-4; see Knapp et al., Wankel et al., Anderson et al., Violaki et al., Markaki et al., etc. -The work of Dyhrman and Van Mooy for DOP use/turnover in the North Atlantic

Minor Comments -Regarding the MUF-P addition: Didn't Martinez and Azam also do multiple additions of L-AMC – how can the authors extrapolate from one 100 μM addition? The present analysis is based on these uptake rates, but they don't show this critical data. Similarly, more information about how the authors calculate the half-saturation constant would be useful – what is the relationship between the DON and DOP uptake rates? This is also fundamental to the data interpretation.

Section 3.3.1: How did the authors eliminate atmospheric deposition as a source of low-d15N N to PNsusp? How do the authors explain the -4 per mil PNsusp d15N without invoking atmospheric deposition or the incorporation of regenerated NH4, and more importantly, what systematic method do the authors use to eliminate whatever process generates the -4 per mil PNsusp d15N from contributing to their other low-

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d15N PNsusp samples?

-Regarding results: Has anyone previously observed [TOP] increasing into the subsurface? It would seem that the TOP values reported here, which are lower in the upper 50 m than below (p. 11-12) may be an artifact of a high blank associated with the SRP measurement (see very recent paper by Patey et al., 2010, Analytica Chimica Acta) – has anyone ever reported [DOP] increasing into the subsurface? I can find no evidence of such a trend in [TOP] with depth – see chapter by Karl and Bjorkman in Hansell and Carlson's Biogeochemistry of Marine Dissolved Organic Matter. If the authors believe their [TOP] data are real, this finding deserves more attention in the manuscript. This seems fundamental to the analysis presented here, and would seem inconsistent with what we know about DOP dynamics in the ocean, i.e., a surface ocean source with consumption at depth. Is the average surface vs. subsurface [TOP] statistically significantly different?

Thought experiment, starting w/ section 3.5.1 - can you show us surface maps of [TON] and [TOP] for each step so we can compare w/ actual distributions? Should we necessarily expect DON and DOP to have similar distribution patterns? Also, please show a plot of TOP concentration vs. artificial age tracer (p. 17, line 25).

-p. 11, line 24: The authors state: "only small vertical gradients in [TON] below 50m"; however, it seems like below 50 m is where the largest changes in [TON] occur. See also Hansell and Carlson, 2001, and Knapp et al., 2005.

p. 13, lines 25-28: The authors argue that the high PNsusp d15N in waters with undetectable levels of NO3 indicates that some source of N other than NO3 must be used to produce PNsusp – but elsewhere they state that winter ML depths in this region are much greater, arguing for enhanced supply of NO3 to surface waters. Why do the authors pick utilization of DON instead of subsurface NO3 as the source of new N in these samples?

p. 18, lines 4-6, p. 19, lines 11-12: Why do the authors invoke N2 fixation and/or

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atmospheric deposition to account for increases in [TON]? What evidence is there for this? Do the authors have rate estimates for the contributions of these processes to the observed concentration? There is evidence from the Sargasso Sea that N2 fixation is NOT capable of changing ambient [DON] (see Hansell and Carlson, 2001; Knapp et al., 2005) – and moreover, simple rate calculations show that regional N2 fixation rates measured with in situ techniques cannot change ambient [DON] on the timescales that surface mixed layers remain isolated for/before winter mixing occurs. The same holds for atmospheric deposition. Please elaborate on this statement; as is, it seems quantitatively implausible. Why not invoke regenerated production/microbial loop?

-There is no evidence, based on concentration data, that DON accumulates in the western oligotrophic gyre (Hansell and Carlson, 2001; Knapp et al., 2005; BATS website)

-The authors estimate that "additional N sources come from the advected DON which has a turnover-time of 6.7 $\pm$ 3 yr"; if this the case, what change in [DON] should be observed? I would guess that the authors would not observe any drop in DON concentration – this seems inconsistent w/ their explanation.

-p. 3, line 18: Hansell et al., 2007, do not suggest that atmos dep of N can resolve the N Atl C imbalance, nor can the magnitude of atmospheric N fluxes account for the C imbalance (see Knapp et al., 2005)

-Knapp et al., 2005, shows that deep NO3 d15N in the N Atl is $\sim$ 4.6 to 5.0 per mil, not 6.0 per mil

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Interactive comment on Biogeosciences Discuss., 7, 4001, 2010.