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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.

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We thank the reviewers for their very constructive comments which will greatly improve the quality of our manuscript.

Anonymous Referee #1

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 per-

haps 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 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.

Reviewer 1

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 sup-

porting >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.

Response

We regret the presence of misleading statements in the manuscript, these will be fully clarified in the revised text. Our line of thinking is the following: dissolved organic nutrients are mainly biologically produced by a variety of mechanisms, which include: active and passive bacterial and phytoplankton exudation, sloppy feeding, viral lysis, particle dissolution. These process are all biomass dependant processes thus, increased biological net DON and DOP production and accumulation occur in regions where biomass and productivity are high, being supported by the presence of inorganic nutrients (eg. Hansell & Waterhouse 1997, Libby & Wheeler 1997, Bronk 2002). It has been hypothesized that these species can then be transported into the oligotrophic gyres where they may fuel autotrophic growth and support new production (Williams & Follows 1998). This hypothesis is supported by DON and DOP large scale patterns (Hansell and Waterhouse 1997, Libby and Wheeler 1997, Vidal et al. 1999, Abell et al. 2000, Mather et al. 2008, Torres-Valdés et al. 2009). The supply of organic nutrients, accumulated in nutrient-rich (non-oligotrophic) waters, to the oligotrophic gyre is the basic assumption of modeling studies that assessed the role of advected DOM as a source of new nutrients (Williams & Follows 1998, 2003, Roussenov et al. 2006, Charria et al. 2008, Torres-Valdés 2009).

As we are interested in the net fluxes of nutrients (organic and inorganic) that can drive new production in the oligotrophic gyre, we want to focus our attention on the net fluxes of DON and DOP that are externally provided to the oligotrophic system (allochthonous supply) i.e. advected/transported from the inorganic nutrient-rich surrounding areas into the oligotrophic gyre rather than onto the local DON production-consumption cycle that support regenerated production. In order to do so we seek help from a model from

which we derive the advection timescale of waters from nutrient-rich areas (where the net accumulation of DON and DOP is likely to occur) to the oligotrophic gyre. Oligotrophic waters, with low nutrient supply, can support only low phytoplankton biomass. These waters have been defined by chlorophyll a concentrations (a proxy of phytoplankton biomass) generally lower than 0.1 mg m^{-3} (eg. Carlson et al. 1977, Antoine et al.1996). This chlorophyll threshold in our model is used to distinguish between oligotrophic waters (where DON and DOP net production is limited) and non-oligotrophic waters (where the net production/accumulation of DON and DOP is fuelled by primary production). However, to investigate the sensitivity of our model results to this threshold, in the revised version we will explore additional thresholds. This will give an estimate of the errors associated with the choice of the 0.1 mg Chla m^{-3} threshold. We hope that it is now clear that this threshold has been used only in the model to estimate the time elapsed, since water parcels left non-oligotrophic regions. In the revised version we will make it more clear that (1) No biogeochemical model is used (i.e. we do not model DON and DOP explicitly). The ocean circulation model (including the artificial age tracer) is only used to derive an estimate of "how long it takes a water parcel to get from outside the oligotrophic gyre to a location along 24.5˚N " (2) This model-based time estimate is not used to infer DON and DOP turnover rates. The model-based time estimate is only compared with DON and DOP turnover rates, which are inferred from the enzymatic cleavage rates. The question we want to address is: if the advection of water from nutrient-rich areas into the gyre core takes from 1-6 yrs (model estimate), can this process be a source of new DON and DOP, within the gyre, given their turnover (enzyme cleavage rates estimate)?

Reviewer 1

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 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 PNsusp 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 sourceof 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?

Response

We are aware that the isotopic evidence presented in the manuscript is not fully sufficient to discriminate between different N sources to PON_{susp} pool. However, we infer this information from the combination of several proxies: surface mixed layer depth and its seasonal amplitude of the seasonal cycle, water temperature, chlorophyll, phytoplankton pigments, inorganic nutrients and DON and DOP gradients, δ^{15}N PON_{susp} and modeled age tracer distribution. This ensemble of observations, put into the context of the prevailing three-dimensional circulation, suggests 4 differently functioning systems. Further, three of the isotopic homogeneous zones are statistically different (Fig. 1 atteched to this rebuttal).

In the western sector of the oligotrophic gyre (70° - $46°$W) the multiple sources of low-

δ^{15}N (N_2 fixation, atmospheric deposition and regenerated NH_4^+) may all be significant. However, the combined observations of a shallow MLD (26 $\pm$ 14 m), elevated water temperatures ($23.9 \pm 0.8°$C), the lack of seasonality of the MLD (quasi-permanent stratification) together with the accumulation of TON relative to TOP, gradients of TOP suggesting its consumption and surface APA activities, suggest that N_2 fixation leads to the observed depleted δ^{15}N PON_{susp}. This is in line with nitrogen-fixing cyanobacteria occurring extensively within the stratified warm waters of the North Atlantic subtropical gyre (eg. Capone et al. 2005, Montoya et al. 2007) being a significant DON source (Capone et al. 1994, Gilbert $\&$ Bronk 1994) and, being adapted for scavenging P from organic matter (Dyhrman et al. 2006) for which they may substantially contribute to the total APA in the water (Sohm & Capone et al. 2006). Although atmospheric N deposition cannot explain the TOP surface consumption its contribution to the low δ^{15}N PON_{susp} and to the TNxs signal cannot be ruled out (as reviewer 1 suggests in a later comment). Thus, in section 3.3.1 of the manuscript we will recalculate the contribution of N_2 fixation based on the assumption that 20 to 35% of the low isotopic signal may be accounted for by TN wet atmospheric deposition (Knapp et al. 2010).

We agree with the reviewer that there may be some isotopic fractionation during DON consumption (Mako et al. 1987, Waser et al. 1998), this is however (to our knowledge) poorly quantified. Nevertheless, our findings of δ^{15}N $PON_{susp} < 4.1$‰ in areas where TON is suspected to act as a N source are not in contrast with an hypothetical DON fractionation. For example, let us assume that DON is consumed and the N is then assimilated into PON_{susp}. As the isotopically depleted DON fraction is suspected to be preferentially consumed (Meador et al. 2007), we would expect the observed δ^{15}N PON_{susp} pool to be lower than the δ^{15}N DON (4.1‰) reported for the North Atlantic (Knapp et al. 2005) which is what we observe.

Reviewer 1

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 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.

Response

We are aware that there is no straightforward method available to infer DOM turnover rates and that all methods have their drawbacks. We will more clearly state the limitations of the enzymatic methodology and in particular of the use of L-AMC. However, as we are assuming that the hydrolysis of DON and DOP are only contributing to export production, which is likely unrealistic, what we are determining is the maximum potential contribution of organic nutrients to new production; thus should the bulk DON have longer turnover rates than our L-AMC estimates, our maximum estimate would not be affected. We will state this limitation more clearly in the revised manuscript.

Reviewer 1

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

Response

Some of these references will be included where appropriate.

Reviewer 1

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 M 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 halfsaturation constant would be useful – what is the relationship between the DON and DOP uptake rates? This is also fundamental to the data interpretation.

Response

Martinez and Azam, 1993 performed multiple L-AMC substrate additions (2 to 200 μM) and measured substrate affinities (K_m) only in axenic cultures of two *Synechococcus* strains; however, they performed only single L-AMC substrate additions (100 μM final concentrations) in seawater samples.

To derive realistic activities based on the ambient concentrations of the substrate, V_{insitu} , ($V_{\max}$ is measured at saturating substrate levels) and realistic turnover, t, based on natural concentration of the ambient pool of DOM from the equations:

$$V_{insitu} = V_{max}S/(K_m + S)$$

t = $[DOM]/V_{insitu}$

the measurement of K_m is needed. The use of the equation $t = [DOM]/V_{max}$ would imply that the substrate concentration [DOM] was present at saturating levels (100μM). Unfortunately we did not perform multiple substrate additions and could not measure the K_m. Therefore, we exploited the empirical relationship between the K_m and the corresponding V_{max} observed in an indipendent Atlantic AMT spring dataset. Given this relationship, we estimated K_m values from our set of measured V_{max} . In order not to run into a circular problem (K_m not independent from V_{max}) and given the high sensitivity of V_{insitu} to K_m changes we estimated the range of all possible V_{insitu} using the minimum and the maximum of the estimated K_m values and not the locally estimated K_m. The so derived range of V_{insitu} were then used to estimate the range of possible turnovers in combination with the ambient DON and DOP concentrations. No statistical correlation was observed between DON and DOP uptake. We will improve the respective section of the manuscript accordingly.

Reviewer 1

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 otherlow-d15N PNsusp samples?

Response

The reviewer is right to say that atmospheric deposition should be invoked to explain the -4 ‰ , in fact this has been stated (pg 4023, line 15-18) and not a-priori excluded as a potential low-δ^{15}N source. We will make this more clear and in section 3.3.1 we will assume that 20 to 35% of the low isotopic signal may be accounted for by TN wet

atmospheric deposition, as estimated by a recent study (Knapp et al. 2010).

Reviewer 1

-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?

Response

The reviewer is right in pointing out that DOP concentrations in Karl & Bjorkman 2002 (their Figs. 10 - 11) are, on average, lower at depth than at the surface. However, despite the low vertical resolution (0-5000m) of these plots, DOP concentrations do not always increase monotonically with depth in the upper 400m. Data with increased vertical resolution presented in Vidal et al. 1999 and Torres-Valdés et al. 2009, do also include profiles where DOP features local maxima within in the upper couple of hundred meters. These observations, put into the context of the prevailing three-dimensional circulation (where lateral processes are not ignored) are not in contrast with the concept of a surface ocean DOP source. In fact our observations are consistent with a surface TOP source outside the oligotrophic gyre and a TOP sink (surface consumption by phytplakton and/or bacteria) within the gyre (Williams & Follows 1998, Roussenov et

al. 2006, Charria et al. 2008, Torres-Valdés et al. 2009).

We do realize that the description TON and TOP leads to misinterpretations and we will put more effort in describing the zonal and vertical gradients and how these are consistent with existing hypothesis on DOM cycling.

As far as we understand Patey et al. 2010, the methodological interference of SRP with arsenate (we assume the effect of to silicate negligible in the oligotrophic surface waters) would result in a spurious, monotonic, increase of SRP and TP with depth; thus, it is unlikely it may produce spurious local maxima of DOP given that the DOP=TP-SRP. Hence, we have confidence in our DOP data.

Reviewer 1

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).

Response

As outlined above, our model is an ocean circulation model and does not include DOM compartments, thus we won't be able to show modeled DON and DOP distribution maps. We apologize for the convoluted language and structure in section 3.5.1. We will provide a revised version which will include schematics of TON and TOP distributions for the idealized scenarios of increasing complexity. Starting from the simplest case of physical control only where TON and TOP (i.e. no active biological production and consumption within the gyre) are advected around the gyre, it is reasonable to expect similar TON and TOP distributions. We do not expect to see similar patterns for TOP and TON in the more complex scenarios, which involve biological DOM consumption and ultimately biological DOM production. This is for a variety of reasons including differing remineralization time scales and nitrogen fixation/atmospheric deposition. The

complexity of the system is well expressed by the TOP and TON concentration vs. artificial age tracer plots (appended to this rebuttal, Fig.2) and will be more carefully outlined in the revised manuscript.

Reviewer 1

-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.

Response

True, this will be corrected in the revised text.

Reviewer 1:

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?

Response

We will remove the inaccurate statements on page 13, lines 22-28. Further, we will clarify that as the isotopic PON_{susp} signal integrates over time-scales longer than the synoptic NO_3 measurement, it is not possible to interpret the isotopic PON_{susp} signal from the nutrient concentrations.

Reviewer 1

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

Response

We have not measured neither N_2 fixation nor atmospheric deposition estimates. In the western ultraoligotrophic portion of the gyre, to explain the local accumulation of 2.9 mmol m^{-3} TON (relative to the 100 m TON average 4.3 mmol m^{-3}) by the microbial loop one would need to invoke a 'malfunctionig microobial loop" (Thingstad et al. 1997) and/or the accumulation of recalcitrant DOM (Carlson et al. 1998). However, there is no longitudinal difference in other biogeochemical parameters that can support this hypothesis and justify such lability gradients. Instead, several studies have shown that N_2 fixation (Capone et al. 1994, Gilbert & Bronk 1994, Karl et al. 1992) and atmospheric deposition (Cornel et al. 1995) are significant sources of DON in oligotrophic systems. Although the fate of the DON derived from N_2 fixation is not well known (Meador et al. 2007, Mulholland et al. 2007 Knapp et al. 2005) it will, locally, enhance the TON pool either as DON (eg. direct release of amino-acids Capone et al. 1994, Gilbert & Bronk 1994) or PON (diazotrophic biomass).

Please note that the zonal TON variability observed in this study is higher than the seasonal variability at the BATS site, while on the other hand, the timescales that surface mixed layers remain isolated is longer (or disturbances are lower in their magnitude). We are aware that at BATS the lack of seasonal and vertical DON gradients (Hansell

& Carlson, 2001, Knapp et al. 2005) together with the seasonal isotopic δ^{15}N DON stability (Knapp et al. 2005) have been interpreted as sign of a static refractory DON pool; and that, one-dimensional (vertical) isotopic balances suggest that N_2 fixation is not a dominant source of N at BATS (Knapp et al. 2005, Altabet 1988). However, recent studies highlighted, given the enriched isotopic signatures of the waters imported in the North Atlantic, the necessity of low-δ^{15}N inputs to explain the thermocline depleted δ^{15}N NO_3 signal (Knapp et al. 2008). Similary, waters fed to the North Atlantic carry a low TNxs signal implying the build up of high TNxs occurring within the North Atlantic subtropical gyre (Landolfi et al. 2008). These observations are in line with the hypothesis that N_2 fixation and/or atmospheric deposition are major N sources. Further indications come from a recent C budget of the Eastern Subtropical North Atlantic by Kähler et al. 2010.

At BATS, lack of gradients in TON measurements imply that the local rate of N_2 fixation are low as compared to the horizontal and vertical physical processes, which homogenize the TON pool. The BATS site is located at the northern boundary of the subtropical gyre where a pronounced seasonal cycle drives a MLD cycle with amplitudes exceeding 200m. In contrast, our study area is characterized by much weaker seasonal MLD cycles. This holds especially for the region where we infer local N_2 fixation. There, the amplitude of the seasonal MLD cylce is less than 100m. Further, N_2 fixation rates increase meridionally towards the tropics (Capone et al. 2005, Montoya et al. 2007). Thus, it is reasonable to expect TON accumulation locally enhanced by N_2 fixation or atmospheric deposition over our region of sampling.

Reviewer 1

-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.

Response

A simplistic crude calculation, assuming that (1) the TON gradients are caused only by biological consumption and (2) vertical processes are negligible as compared to horizontal transport (3) that no mixing with other water masses occurs, suggests a TON decrease of ca 1 mmol m^{-3} over one year. Given the West-East differences in the modeled advection time-scales ($>$ 1 year), this TON decrease could explain the observed TON zonal gradient (Δ 0.7 mmol m^{-3}).

Reviewer 1

-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)

Response

Will be corrected

Reviewer 1

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

Response

Will be corrected

Anonymous Referee #2

Reviewer 2

The authors present a number of observational and modeling results related to the question of elemental cycling in the oligotrophic part of the North Atlantic. They setout to "assess the potential of DON and DOP to explain the [...] carbon and nitrogenbalances", but I found it very difficult to see whether the paper comes anywhere near attaining this goal.

The manuscript has no clear focus and is therefore often difficult to follow.

Response

We will put more effort in describing the focus of the paper.

Reviewer 2

In several places there is a lack of scientific scrutiny and precision, e.g., the analysis rests on the implicit assumption that ammonium is negligible, but this his nowhere stated or demonstrated.

Response

Ammonium concentrations are very low in the oligotrophic regions (Brzezinski 1988). This is due to the highly dynamic behavior of ammonium uptake and release, which drives the oligotrophic spinning wheel (regenerated production, Goldman 1984). Thus, standing stocks of ammonium may be regarded as neglectable in ogliotrophic gyres. This will be clarified in the text.

Reviewer 2

Most importantly, several of the assumptions are likely to be unjustified, e.g., that significant net production of DON and DOP occurs only at the surface and when chlorophyll concentrations exceed 0.1 mg m^-3. As oligotrophic regions frequently feature

subsurface phytoplankton biomass layers and production, this is a highly questionable assumption. As a consequence, it is not clear to me what we can learn from this study.

Response

We will fully clarify this assumption. Dissolved organic nutrients are mainly biologically produced by a variety of mechanisms, which include: active and passive bacterial and phytoplankton exudation, sloppy feeding, viral lysis, particle dissolution. These process are all biomass dependant processes thus, increased biological net DON and DOP production and accumulation occur in regions where biomass and productivity are high, being supported by the presence of inorganic nutrients (Hansell & Waterhouse 1997, Libby & Wheeler 1997, Bronk 2002). It has been hypothesized that these species can then be transported into the oligotrophic gyres where they may fuel autotrophic growth and support new production (Williams & Follows 1998). This hypothesis is supported by DON and DOP large scale patterns (Hansell and Waterhouse 1997, Libby and Wheeler 1997, Vidal et al. 1999, Abell et al. 2000, Mather et al. 2008, Torres-Valdés et al. 2009). The supply of organic nutrients, accumulated in nutrient-rich (non-oligotrophic) waters, to the oligotrophic gyre is the basic assumption of modeling studies that assessed the role of advected DOM as a source of new nutrients (Williams & Follows 1998, 2003, Roussenov et al. 2006, Charria et al. 2008, Torres-Valdés 2009).

As we are interested in the net fluxes of nutrients (organic and inorganic) that can drive new production in the oligotrophic gyre, we want to focus our attention on the net fluxes of DON and DOP that are externally provided to the oligotrophic system (allochthonous supply) i.e. advected/transported from the inorganic nutrient-rich surrounding areas into the oligotrophic gyre rather than onto the local DON production-consumption cycle that support regenerated production. In order to do so we seek help from a model from which we derive the advection timescale of waters from nutrient-rich areas (where the net accumulation of DON and DOP is likely to occur) to the oligotrophic gyre. Oligotrophic waters, with low nutrient supply, can support only low phytoplankton biomass.

These waters have been defined by chlorophyll a concentrations (a proxy of phytoplankton biomass) generally lower than 0.1 mg m^{-3} (eg. Carlson et al. 1977, Antoine et al.1996). This chlorophyll threshold in our model is used to distinguish between oligotrophic waters (where DON and DOP net production is limited) and non-oligotrophic waters (where the net production/accumulation of DON and DOP is fuelled by primary production). However, to investigate the sensitivity of our model results to this threshold, in the revised version we will explore additional thresholds. This will give an estimate of the errors associated with the choice of the 0.1 mg Chla m^{-3} threshold. We hope that it is now clear that this threshold has been used only in the model to to estimate the time elapsed, since water parcels left non-oligotrophic regions.

Reviewer 2

The manuscript fails to conclusively answer the question posed in the introduction. The conclusions are either vague, dominated by "appear to be", and "suggest that", or overreach what can be derived from the material. Finally, submitting a manuscript containing so many (mostly avoidable) typographical errors and other demonstrations of carelessness shows a certain degree of disrespect towards readership and reviewers (Remember: "Why should anyone else care about the manuscript if the authors don't".)

A (probably incomplete) list follows:

page 4002, line 13: western (not wester)

page 4002, line 15: stimulates (not stimulate)

page 4005, line 5: ... we want to (1) assess ... (2) investigate (not want to assess (1)

... and (2) investigate)

page 4005, lines 7 and 15: assess (not asses)

page 4006, line17: particulate matter is considered negligible. Does this refer to "inor-

ganic"

species only?

page 4015, line 25: Fig. 10 (not Fig. 9)

page 4017, lines 15/16: Does this refer to Fig. 4?

page 4017, line 27: than (not then)

page 4019, line 24/25: turnover rates have units of 1/time and not time

page 4020, line 1: yielded an average (not yielded a an average)

page 4020, line 3: greater than (not grater then)

page 4020, line 8: allochthonous (not allochtonus)

page 4020, line 18: than (not then)

page 4021, line 7: allochthonous (not allocthonus)

page 4022, line 6: Gulf Stream (not gulf stream)

page 4025, line 8: Gulf Stream (not gulf stream)

Response

We thank the reviewer for these detailed comments; all these typographical errors will be corrected.

Reviewer 2

I also oppose the use of popular "buzz words" in inappropriate ways: the term "regime shift" (page 2025, line 10) usually refers to a "rapid temporal reorganization of a system from one relatively stable state to another", but not to spatial variations that are interpreted as different dynamical regimes in neighboring regions.

Response

Here we meant to express the “change of the controlling conditions” (regime: from Latin regere = regulate, control), which can apply also to a spatial and not necessarily to temporal domains. However, as it may be confused with “temporal variations” we will correct it in the revised text.

Anonymous Referee #3

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Reviewer 3

The manuscript deals with organic nutrients as sources of N and P to the upper layer of the North Atlantic. To this end, authors introduce the two main topics to tackle with: (1) the missing nutrients for export production in the oligotrophic subtropical Atlantic and (2), the significance of the dissolved forms of nutrients in balancing the mismatch between import-export nutrients. To be able to sustain primary production and contribute to the export production, these organic nutrients have to be labile but not much, as to be transported from the nutrient rich / production sites to the oligotrophic sites. This is the core issue, and although the idea might be appealing, the manuscript does not contribute to its resolution.

One main problem is the definition of the sites of net dissolved organic nutrient production. The other is the computation of the transit time of those nutrients. With respect to the former, authors offer no convincing evidence to justify their choosing of the 0.1 mg chl a / m3 as a threshold for net production of organic nutrients.

Response

We will fully clarify this assumption. Dissolved organic nutrients are mainly biologically produced by a variety of mechanisms, which include: active and passive bacterial and phytoplankton exudation, sloppy feeding, viral lysis, particle dissolution. These process are all biomass dependant processes thus, increased biological net DON and DOP production and accumulation occur in regions where biomass and productivity are high, being supported by the presence of inorganic nutrients (Hansell & Waterhouse 1997, Libby & Wheeler 1997, Bronk 2002). It has been hypothesized that these species can then be transported into the oligotrophic gyres where they may fuel autotrophic growth and support new production (Williams & Follows 1998). This hypothesis is

supported by DON and DOP large scale patterns (Hansell and Waterhouse 1997, Libby and Wheeler 1997, Vidal et al. 1999, Abell et al. 2000, Mather et al. 2008, Torres-Valdés et al. 2009). The supply of organic nutrients, accumulated in nutrient-rich (non-oligotrophic) waters, to the oligotrophic gyre is the basic assumption of modeling studies that assessed the role of advected DOM as a source of new nutrients (Williams & Follows 1998, 2003, Roussenov et al. 2006, Charria et al. 2008, Torres-Valdés 2009).

As we are interested in the net fluxes of nutrients (organic and inorganic) that can drive new production in the oligotrophic gyre, we want to focus our attention on the net fluxes of DON and DOP that are externally provided to the oligotrophic system (allochthonous supply) i.e. advected/transported from the inorganic nutrient-rich surrounding areas into the oligotrophic gyre rather than onto the local DON production-consumption cycle that support regenerated production. In order to do so we seek help from a model from which we derive the advection timescale of waters from nutrient-rich areas (where the net accumulation of DON and DOP is likely to occur) to the oligotrophic gyre. Oligotrophic waters, with low nutrient supply, can support only low phytoplankton biomass. These waters have been defined by chlorophyll a concentrations (a proxy of phytoplankton biomass) generally lower than 0.1 mg m^{-3} (eg. Carlson et al. 1977, Antoine et al.1996). This chlorophyll threshold in our model is used to distinguish between oligotrophic waters (where DON and DOP net production is limited) and non-oligotrophic waters (where the net production/accumulation of DON and DOP is fuelled by primary production). However, to investigate the sensitivity of our model results to this threshold, in the revised version we will explore additional thresholds. This will give an estimate of the errors associated with the choice of the 0.1 mg Chla m^{-3} threshold. We hope that it is now clear that this threshold has been used only in the model to trace water parcels that had left non-oligotrophic regions.

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...Respect to the later, I have the impression that analytical problems and the various assumptions involved in the computation of turnover times of both DON and DOP may cast doubt on data. I refer to the different efficiencies in DOM oxidation used for DON (HTCO) and DOP (photooxidation) determinations, yielding different percentages of the total pools accounted for N and P; and to..

Response Preliminary tests with standard compounds were carried out to evaluate the efficiency of the UV oxidation method (Landolfi et al. 2005). The resulting N and P recoveries were 79$\pm$0.4% and 94$\pm$1.8% respectively. Further, in all our field samples, the UV lamp oxidation efficiency was checked at every oxidation using a model compound (adenosin-5monophosphatemonohydrate AMP; Kerouel and Aminot 1996). The recovery of the AMP compound was 94 % of P and only 60 % of N. Given the low N recoveries yielded by the UV oxidation we decided to use the HTCO oxidized TON samples for our analysis. It is known that the HTCO method has higher TON recoveries with respect to the UV oxidation method (Bronk et al. 2000). With this latter method the oxidation efficiency ranged from 96 - 100%. Thus, the TON and TOP oxidation efficiencies of our samples are comparable and are grater than 90%. We will address this issue more explicitly in the manuscript.

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...the authors assumption that those pools are accessible to the enzymes, excluding the possibility of different degrees of lability for DON and DOP molecules.

Both facts have an effect on the computation of in situ enzyme activities in different ways for N and P so resulting in uncertainties in the calculated turnover times.

Response

The reviewer is right regarding the limitations of the enzymathic method used and the implications for the turnover estimates, this will be stated more clearly. It must be said that DOP vertical gradients suggest that most of the DOP in surface waters is labile and

reactive (eg. Suzumura and Ingall 2004) whereas instead not all of the surface DON is reactive. Hence, should the DON reactive pool be smaller than our measured bulk DON surface pool, our turnover estimates would be conservative estimates. However, we gain additional confidence in our turnover calculations as these are within 10% of the turnover calculated using the approach of Mather et al. 2008. Their method derives the turnover rates from: $t = K_m/V_{max}$ which does not involve ambient DON and DOP concentrations.

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The analysis of the isotopic signal of particulate organic nitrogen (PON) constitutes the other important part of the manuscript. This is surprising because this issue is barely mentioned in the introduction. Otherwise, the interpretation of results of the isotopic PON signal is plagued of inconsistencies. For instance, equivalent isotopic values in western (to about 70_ W) and eastern (46-30_ W) parts are interpreted as indicating the presence of inorganic nutrients in the former case, and the lack of measurable nitrate in the later (page 4013, line 21 and onwards). This is at odds with the nitrate distribution of figure 3, page 4034, which shows lower nitrate concentrations in western than eastern parts.

Response

We will correct the inaccuracies related to the description of PON_{susp} isotopic signals (page 4013, line 21). We will clarify that the isotopic PON_{susp} signal cannot indicate the presence of a specific N source at the time of sampling as it records the N sources of the recent past. Further, as low stocks of a specific nutrient (e.g. NO_3) are not necessarily related with low nutrient fluxes, we will not infer any information from nutrient concentrations to explain the observed isotopic signatures.

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Other objection with this manuscript refers to the interpretation of DON and DOP dis-

tributions in relation to the hydrographical setting (section 3.1, page 4011). I would like to see some comment on the relationship between the mixed layer depth, the depth of the nutricline, and chlorophyll depth distribution. The fact is that the higher DON in the west than in the east, as stated by the authors (Page 4011, line 22), coincides with a greater separation between the MLD and the nutricline depth and, as a consequence, low chlorophyll a concentrations in the mixed layer. In contrast, in the eastern parts the nutricline overlaps the MLD, so contributing more nutrients to the mixed layer and more chlorophyll a. This contradicts the author's appreciation concerning the regions of net organic nutrient production. DOP concentrations show the reversed pattern, with high concentrations in the east and very low values in the west. I wonder if these different patterns are a consequence of the methodological constraints before stated, i.e. the inefficiency of the DOP oxidation procedure. Authors, have also to explain the subsurface DOP increase observed in the central parts.

Response

We will describe better the physical factors in relation to the DON and DOP distribution. It is for the complexity of such data that we seek auxiliary help from ideal scenarios and model age tracer estimates. The accumulation of TON in the permanently stratified western oligotrophic gyre is consistent with observations of enhanced N supply from N_2 fixation and/or atmospheric deposition. Instead, DOP distribution pattern is consistent with the lack of external DOP sources, such as N_2 fixation and atmospheric deposition for the N pool, and its biological consumption along the gyre scale circulation.

As stated above our oxidation efficiency is grater than 90% for both our TON and TOP samples. Thus, we are confident about our data, notwithstanding we believe it is highly unlikely that DOP inefficient oxidation would exhibit a zonal gradient.

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The ensemble of problems stated above is not helpful for the interpretation of data and do not contribute to provide reliable conclusions. This in turn affect to the definition

of the four regions characterized by different nutrient supply regimes (page 4002, line 8), which authors typify on the basis of the isotopic PON signature, dissolved organic nutrient distributions, mixed layer depth, etc. (page 4022), and raise as one of the main conclusion of the manuscript.

In summary, I consider that this manuscript do not provide with reliable data to answer the three main questions rose in the introduction (page 4005, line 5), in part because data interpretation and most assumptions are not justified. With reference to more formal aspects, the manuscript is poorly structured and written, and plagued of mistakes and inconsistencies. I consider that the manuscript is not acceptable to be published in Biogeosciences journal.

Response We hope, based on the three reviews, we have identified the misleading sections. We propose to make a substantial revision of the manuscript.

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Caption of Fig. 1: Boxplots of the $\delta PO^{15}N$ in four different regions. The plot displays the distribution of the samples around their median. The heights of the notches in each box are computed so that the side-by-side boxes have non-overlapping notches when their medians are different at a default 5% significance level. The whiskers indicate the observations that are above the 25th and 75th percentile. Comparing the median of the adjacent box-plots provides a visual hypothesis test analogous to the t test. The null hypothesis of equal medians can be rejected in the three western most regions. Instead, the medians of the regions 46-30˚W and 30-10˚W are not statistically different.

Caption of Fig. 2: Observed organic nutrients (along 24.5˚N) at the surface (upper 100 m) versus modeled transit time (the time elapsed since water parcels left non-oligotrophic regions). Upper (lower) panel refers to total organic nitrogen (phosphorous). Please note that the highly dynamic regions (affected by seasonal variability) are characterized by transit times estimates $<$ 1 years.

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

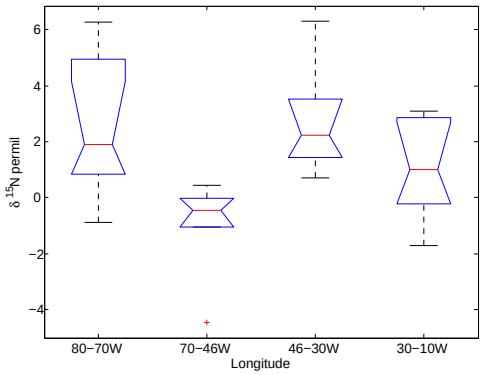

Fig. 1.

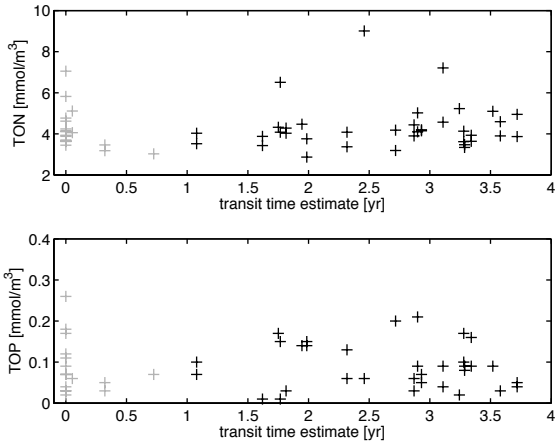
TON [mmol/m3]
transit time estimate [yr]
TOP [mmol/m3]
transit time estimate [yr]

Fig. 2.