

Interactive comment on “Stoichiometries of remineralisation and denitrification in global biogeochemical ocean models” by A. Paulmier et al.

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Reply to Referee 1:

We thanks the referee for her/his very thoughtful and constructive comments that, we think, greatly helped us to improve the manuscript. Following the suggestions of the referee, we have made considerable changes which are presented in detail in the text below. All reviewer comments are in italics, whereas our response/action is described in roman font.

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MAIN COMMENTS:

1) *Paulmier et al.* show, based on the manipulation of stoichiometric equations representing different pathways of organic matter remineralization, that the amount of oxidant (namely oxygen or nitrate) required to oxidize a given amount of organic matter depends greatly on the amount of hydrogen present in the organic matter. Furthermore, they show that current implementations of a specific set of biogeochemical models do not take this effect into account adequately, which results in inter- and intra-model inconsistencies as to the assumed composition of the organic matter participating in the remineralization process.

That modelers have not explicitly stated hydrogen assumptions until now is unfortunate, but the realization that the hydrogen content of organic matter is an important variable modulating the oxygen demand in the sea is not a new finding. Hydrogen itself is rarely explicitly considered, as hydrogen measurements are quasi inexistent on bulk marine organic matter; Anderson (1995) and Hedges (2002) being notable exceptions. Instead, the effect of hydrogen is often partly captured in the O₂:C ratio, which appears to be more tightly controlled than the C:H ratio for instance (see Laws 1991). As such, a discussion of the O₂:C ratio as it pertains to the equations derived in this manuscript and some indications on how the O₂:C ratio is treated in each model would be an interesting and valuable addition to this manuscript.

We thank the referee for this instructive comment that we are happy to take into account. Specifically, we add some more detailed text in O₂:C and H:C ratios in the presentation of the models (Introduction section), and in the subsections 2.1, 2.2, 3.3.2 and 4.2 concerning the hydrogen assumptions and the O₂:C ratios, respectively (Cf. also in Table 1).

In a subsection of this paper (3.3 – Implications), Paulmier et al. also make interesting claims regarding the cycling of nitrogen in oxygen minimum zones (OMZ). Specifically, they write in section 3.3.2 "How much fixed N is removed during denitri-

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fication": " : : if the newly fixed N is transformed into organic matter above suboxic areas, and upon sinking into the suboxic environment, is denitrified, an addition of new nitrogen at the ocean surface could generate an even greater loss of fixed nitrogen in the suboxic areas below". This statement deserves, in my opinion, further discussion. By the above statement, do Paulmier et al. imply that a sort of accelerating runaway effect exist whereby the ocean would loose its nitrate unless organic matter production above OMZ stopped (at least periodically) or N₂-fixation rates increased? Due to the estuarine circulation cell that broadly characterizes the OMZ, waters upwelling near OMZ are relatively rich in phosphate (low N*) making the environment suitable for N-fixation. As per Paulmier et al, however, this new nitrogen would further increase the N-loss below, and so further lower N* and further encourage N-fixation above OMZ. If true, this mechanism would have important implications and this needs to be recognized. It seems unlikely that the runaway exist, so what could be the processes that limit this effect? Obviously nitrate supply to the OMZ would have to be considered and it implies that it is ultimately the nitrate supply into the OMZ that limits N₂-fixation at the surface. Mass-balance suggests this should be the case.

It seems that there also should be some correspondence between section 3.3.2 "how much fixed N is removed during denitrification" and 3.3.3 "How much N₂ is produced during denitrification". Yet, each section attempts to answer these questions with ratios ($R(N:Norg)$ and $R(N_2:HNO_3)$) that seem unsuited to the questions posed in the subtitles. I think these 2 sections should be revisited.

We re-wrote this part corresponding to the previous section 3.3.2 and 3.3.3 in a new section 3.3.2 taking into account the comments of Referee 1 and merging the results from sections 3.3.2 and 3.3.3. The speculations about a possible accelerating runaway effect for the N loss in the OMZs is based on the results from a box model study by Canfield (2006). This will be presented in more detail in the revised paper. According to that model, which assumes a local coastal upwelling cell, a runaway effect is not possible without nitrogen fixation. Under these circumstances nitrate becomes the limiting nutrient eventually reducing export production and subsequent

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nitrogen removal in the OMZ. When nitrogen fixation is allowed for in the model, a runaway effect is possible. Canfield (2006) discusses possible causes of the apparent lack of this runaway effect in today's ocean, including too high nitrate concentrations in the upwelled waters and to low light levels in turbid coastal waters. We add some discussion of this and also speculate the spatial organisation of ventilation/upwelling pathways may be critical for the observed inexistence of the speculated runaway effect.

SPECIFIC COMMENTS:

Section 1.

"Much of the paragraph between lines 9-24 of page 2542 describing the model could be split under the appropriate bullet points above that paragraph. Rather than emphasizing the origins of these models, this paragraph should emphasize the assumptions made regarding the assumed stoichiometry.

We reworked the presentation of the different models accordingly, emphasizing their similarities and differences, especially concerning the main assumptions concerning the stoichiometry.

Section 2.

If phosphorus is present as nucleic acid, phospholipids, etc. what is the rationale for using the form H₃PO₄?

The choice to use the form H₃PO₄ derived from the fact that the BGC models are usually assuming phosphorus to be present as phosphate and not nucleic acid, phospholipids, etc... As the main goal of this study is to compare the impacts of the different stoichiometries considered in the BGC models, we decided to use the common model assumption. We add one additional sentence in this sense in subsection 2.1.

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In section 2.1.2, NH₃ does not “dissociate” into NH₄⁺.

We agree with the reviewer that our sloppy wording was incorrect and that NH₃ does not “dissociate” into NH₄⁺. What we wanted to refer to and clarify in the revised version is that NH₃ produced during protein hydrolysis reacts with water and under cell pH as well as oceanic pH immediately dissociates into NH₄⁺. In strictly chemical sense, in aqueous solution, ammonia deprotonates some small fraction of the water to yield ammonium (and hydroxide OH⁻).

The title for subsection 2.1.3 is awkward. Maybe use simply “Carbon, hydrogen and the oxygen demand for remineralization”. It maybe relevant to discuss the results of Laws (1991) and Hedges (2002) in that section also. The subsections in section 2 are usually 1 sentence. The use of these very small subsections breaks the flow of the paper.

For section 2, we removed the 3 different subsections (including the once with the awkward title) into one subsection 2.1 with the simple title (“Classical notation”). In this subsection 2.1, and also 2.2 and 3.2.2, we added some discussions, especially about the results of Laws (1991) and Hedges (2002). Cf. also in Table 1.

Sections 3 up to 3.2 is very didactic and generally clear. The reasoning for not accounting for the anammox reaction in section 3.2.2 is not clear to me, however.

The reasoning for not accounting for the anammox reaction in section 3.2.2 was mainly based on the fact that none of the BGC models is explicitly considering this bacterial process, and the manuscript will become too long. However, it appears to us to be important to mention this process, since the parameterization of the coupling between anammox and other process as denitrification or nitrification could have significant impact on the global biogeochemical cycles.

Why prefer equation 16 proposed by Richards (1965) when evidence for this reaction has not been found?

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The equation 16 proposed by Richards (1965) is mentioned because this is the equation implicitly used in the BGC models to convert the ammonium produced by anaerobic remineralization (nitrate-respiration) into N_2 (See additional comment in subsection 3.2.1). This reasoning is now explained in more detail in the text.

Also, move the sentence "Note, that the C/N/P stoichiometries..." of section 3.1.3 after the second example.

We agree with Referee 1 and moved the sentence "Note, that the C/N/P stoichiometries..." to the end of the section 3.1.3.

Change "oxix" to "oxic" in section 3.3.1, line 23 and clearly state the assumptions made (that is, $a=106$, $b=175$, $c=42$, $d=16$) to compute the example ratio $R(N:Norg)=7$.

We corrected "oxix" into "oxic", and clearly state the assumptions made to compute the example ratio RN:Norg of 7.

Also, correct the error "7 atoms" to "7 moles" right after equation 21.

We corrected "7 atoms" into "7 moles" right after equation 21.

Section 4 is also interesting, even if the interest seems to be largely limited to those people involved to the development of the specific models. Efforts should be made to maintain the fractional rather than the decimal notation in some of the equations, however; this makes it easier to follow for the reader.

We used now the fractional notation for all the equations in Section 4.

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