

Interactive comment on “Feedbacks of CO₂ dependent dissolved organic carbon production on atmospheric CO₂ in an ocean biogeochemical model” by L. A. Bordelon-Katrynski and B. Schneider

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We would first like to thank the Referee for the very thorough and thought provoking comments regarding our manuscript. This carefully written critique has brought to our attention a possible confusion in the focus of our study that we would like to clarify before addressing the specific comments listed below.

The focus of our study is on the mechanism of particle aggregation (Arrigo 2007) not C:N decoupling or carbon overconsumption. Possibly the use of the abbreviation DOC

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rather than DOM was, at points in the text, misleading, and we will use the terms DOC and DOM more carefully in the revised manuscript. Furthermore, we decided to use constant C:N ratios, since several studies have done detailed analyses on the stoichiometry of the dissolved and particulate carbon pools (Riebesell et al. 2007, Engel et al. 2008, Schulz et al. 2008, Kim et al. 2011) and none of them found significant changes in the stoichiometry of either pool in mesocosm studies.

When writing the manuscript we believed that our study was very similar to the study of Tagliabue et al. 2011, who explained that in their PP-DOC experiment the C:N ratios of sinking particles do not change (Table 1 of Tagliabue et al. 2011). However, due to aggregation of carbon enriched DOM, the elemental composition, also of the sinking particles, must have changed (personal correspondence with coauthor L. Bopp). Therefore, the study of Tagliabue et al. (2011) is actually more different to ours than we thought before. In the absence of clear indications for stoichiometric shifts in DOM, both studies serve as ideal complements with regard to the question of the fate of DOM and particle fluxes in the water column under ocean acidification. We will carefully address these issues in our revised version. Consequently, we do not see a need to perform new simulations with decoupled C:N ratios in DOM, which would be the repetition of a well conducted study (Tagliabue et al. 2011). However, we would like to pick up the Referee's suggestions for improvement and conduct further sensitivity analyses, e.g. on the critical thresholds of POC to be exported and of DOC to form POC via aggregation.

REFEREE:

1 General comments

1.1 Summary

In the study of Bordelon-Katrynski and Schneider the PISCES model (model of Pelagic Interaction Scheme for Carbon and Ecosystem Studies) is applied to compute the potential impact of carbon sequestration on global scale, assuming increased dissolved

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organic carbon (DOC) exudation along with a rise in atmospheric carbon dioxide (CO₂) concentration. Results of this specific model setup are compared with results of other model configurations, so that the computed impact of their assumption can be isolated from other (physical-chemical) CO₂ effects. Their model simulation with CO₂-sensitive exudation yields a positive feedback on atmospheric CO₂. This result is contrary to results of Tagliabue et al. (2011), who simulated enhanced export flux with rising CO₂ concentrations. The study of Bordelon-Katrynski and Schneider not only complements but also questions the generality of the model outcome of Tagliabue et al. (2011). In their conclusion they state that the sign of the CO₂ ocean-atmosphere feedback depends on the pathway of excessive carbon uptake.

1.2 Impression after review

I fully agree with the author's notion that magnitude and sign of the feedback depend on the possible pathway chosen for channeling the additional (excessive) carbon uptake. But their conclusive remark does not really help when elucidating global CO₂ flux estimation. It does help, though, to assess alternative model solutions. In their study, the authors intend to provide an alternative solution to Tagliabue et al. (2011), which is desirable and helpful. The question is whether the pathway for excess carbon uptake is plausible or not. The authors have not critically assessed details of their approach and have not discussed the implication of their modified PISCES equations. In the following I will explain why the alternative model setup is implausible. I will also outline the sensitivity to expect from those model equations that describe the dynamics of primary interest: the critical linkage between DOC exudation and export flux of particulate organic carbon (POC) in PISCES. Much to my regret, I must not recommend their study for publication.

2 Specific comments

2.1 CO₂ induced enhancement of DOC exudation, given a constant carbon- to-nitrogen stoichiometry of phytoplankton and particulate organic matter (POM) export

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The author's describe DOC exudation as a proportion (5 %) of net primary production (NPP) in the control run and then infer a transfer function to account for an CO₂ induced increase of exudation to match 20 % of NPP after 140 years after spin-up. The reasoning in taking such an approach can only be understood as to maintain NPP similar to the control run, while all excessively fixed carbon (C:N assimilation ratio higher than 122:16) enters the DOC pool directly. It implies that gross primary production (GPP) and exudation increase in equal amounts in order to have similar NPP values; we have $GPP = \text{exudation} + \text{NPP}$ to keep $NPP = GPP - \text{maintenance respiration} - \text{exudation} \approx \text{constant}$.

So far, it seems to be a smart and fair approach. The additional DOC can then either be respired or is exported via 'aggregation'/adsorption of DOC to detrital and sinking POC (according to equations 4 in Gehlen et al., 2006). In Table 2 we see that after introducing the additional carbon into the system we find an increase (8 %) in NPP together with an increase in surface nitrate concentrations. Ocean mixing and advection are identical. But why do results of NPP change then? The authors wrote: "The changed DOC cycling also affects nutrient distributions with a tendency of shallow water nitrate accumulation, which reduces the vertical NO₃ gradient. Especially around and directly below the subtropical gyres NO₃ accumulates under higher DOC formation (Table 2, Fig. 2e, f)." Changes in NPP are attributed to redistribution, sinking and mineralisation of organic matter. Yes, the formation and sinking flux of POC is altered by an increase in DOC exudation, as defined in equations 4 in Gehlen et al. (2006). I see, however, a problem in that "additional" carbon can enter the two sinking pools (small and large particle aggregates) but the POC pool is then mineralized with a constant N:C ratio of 16:122. The C:N:P composition of dissolved and particulate matter in PISCES is tied to a constant stoichiometry. Therefore, DOC added to the model system introduces an additional source of nitrogen during mineralisation. This is a severe model deficiency, because on the times scales considered here it has an affect on the processes of interest. This situation seems similar to the 'PP-DOC' model run depicted in Tagliabue et al. (2011).

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REPLY: There seems to be a misunderstanding due to the inexact use of 'DOC' in our manuscript which, at times, should refer to 'DOM'. Since we used constant C:N element ratios for DOM, which we can again mention in the method's section for clarity, we implied that any change in DOC would be followed by a proportional change in DON. Consequently, there is no additional nitrogen source in the model during DOM remineralization. We have now also checked the total nitrogen budget ($\text{NO}_3 + \text{NH}_4 + \text{PON} + \text{DON}$) and found it to remain constant in all simulations.

A second misunderstanding seems to be in the use of the term "extra carbon". We consider this term to be the amount of carbon resulting from gas exchange with the atmosphere due to altered DOM formation. We will replace this term with "anomalous carbon" in the new version of the manuscript, because it may also regionally vary between positive and negative values.

NPP increases under higher DOM formation due to the mechanisms explained in the manuscript: shallower remineralization and thus faster turnover of NO_3 . The shallower nutrient turnover is caused by more NO_3 being routed into DON at the expense of PON, due to constant stoichiometry. This shallow remineralized NO_3 is in turn available for PON (POC) formation. Consequently, total NPP is enhanced, and in some regions even enhances particle export.

REFeree: 2.2 Distinction of labile and semi-labile DOC and POC The following model assumptions in this study are arguable:

a) All DOC exuded by phytoplankton is semi-labile and exclusively consists of surface-active compounds that can adsorb to or aggregate with POC (equations 4 in Gehlen et al., 2006). It is difficult to specify qualitative characteristics of the bulk (fresh) DOC pool in the field or laboratory. In a data-model synthesis we estimated changes between $34 \pm 8\%$ (bloom period) and $63 \pm 20\%$ (post-bloom period) of all freshly exuded DOC to consist of surface-active compounds (e.g. acidic polysaccharides, Schartau et al, 2007). These acidic polysaccharides may then act as precursors to form larger macro-

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gels, often measured as transparent exopolymer particles (TEP). Thus a residual fraction of fresh DOC (not refractory!) exists whose fate is undetermined. To impose that all freshly exuded DOC can form TEP is therefore inappropriate.

b) DOC exudation increases with an increase in NPP. This assumption is difficult to justify because many observations show maximum DOC exudation during post-bloom periods, at times when NPP (or relative growth rates) converge towards zero. It is rather a function of the imbalance between photosynthesis and cell growth.

c) Modelled POC:PON remain near Redfield stoichiometry under all growth conditions so that all excessive carbon uptake enters the DOC pool and can form TEP. Data from the mesocosm experiment in Riebesell et al. (2007) show nearly unaltered POC:PON ratios. Their findings are extraordinary, but we have to consider that their hypothesis and interpretation of the experimental outcome had not been confirmed with DOC or TEP data explicitly.

REPLY:

a) We agree that further refinement of the assumptions about fraction and/or temporal evolution of DOC ready to aggregate would be possible. However, we use a rather simplified ocean biogeochemical model to perform a first order sensitivity test on the potential influence of enhanced DOM formation on particle fluxes under ocean acidification. Here, we assume that this more precise defining of DOC would be a limiting rather than an amplifying factor.

b) DOC exudation increases with an increase in NPP. This assumption is difficult to justify because many observations show maximum DOC exudation during post-bloom periods, at times when NPP (or relative growth rates) converge towards zero. It is rather a function of the imbalance between photosynthesis and cell growth.

c) Maybe this point needs to be better clarified in a revised version, but we intended to address it in the introduction pg 7986 lines 1 and 2 that state "The fate of the excess

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carbon remains unknown" and in lines 2 and 3, where we refer to that the in paper by Riebesell et al. 2007 increased formation of DOC and TEP was hypothesized. We agree it is unfortunate that the study by Riebesell et al. (2007) was unable to confirm the location of the extra carbon pool. This is also the reason why we find it justified to keep C:N ratios constant in both particulate and dissolved organic matter.

REFeree: 2.3 The simulated POC export flux is sensitive to the amount of phytoplankton biomass that can be build up, which in turn depends on relative growth rate

Equations 4 in Gehlen et al. (2006) describe the crucial link between DOC and export of POC, the flux from DOC to POC is defined as $\Phi_{DOC} * sh * DOC^2 + \Phi_{DOC} * sh * DOC * POCs$. According to these equations the sensitivity of DOC transformation depends on simulated POCs concentration. In Tagliabue et al. (2011) the POC within the upper layers must be higher than in this study, as global NPP is much higher (49 PgC yr⁻¹) compared to this study's reference run (30 PgC yr⁻¹). A difference in simulated POC must yield a different impact (sensitivity) on the amount of DOC that can be channeled to the model's pool of sinking POC. Provided that same parameter values for Φ_{DOC} and Φ_{DOC} were used in Gehlen et al. (2006), Tagliabue et al. (2011) and in this study, differences in DOC transformation to POC export can be attributed to differences in their simulated POCs concentrations. The build-up of POCs is one critical key to determine whether DOC is eventually exported or can reside in upper layers. In the second paragraph on page 7994 (discussion section) this issue is addressed roughly. The lower preconditioned simulated POCs concentrations the smaller the effect on export and more "additional" DOC will reside in the upper layers, where it can be hydrolyzed and respired (a shallower turnover of organic matter, discussed in the second paragraph on page 7995).

REPLY: We appreciate the suggestion to determine critical threshold concentrations of POC and DOC, as will be explained below.

REFeree: 2.4 Suggestions for improvements Following the discussion section, differ-

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ences in the sensitivity of DOC entering POC export flux had been sensed but were not analyzed further. I suggest that the authors look into details of this flux, explaining why some regions have an enhanced C-export whereas others reveal higher DOC concentrations within the upper layers. This analysis would give some insight to a critical POCs mass to enhance DOC transformation and to eventually foster export flux. How large must DOC and POCs concentrations be to enhance export flux of the "additional" DOC? I also think that the additional carbon uptake should be traced by an increase in the C:N ratio of exported particulate matter. This can possibly be achieved even when primary production is assumed to maintain a constant C:N:P stoichiometry. A sensitivity analysis of the pathways of excessive DOC production should also consider differences in global NPP. At which NPP (e.g. changing maximum growth rates) does the model switch from an overall positive feedback to a negative feedback? Finally, I strongly recommend to compute the nitrogen budgets (combining NO₃, NH₄ with the organic carbon mass converted to nitrogen with the assumed elemental ratio of 122:16) and control mass conservation of the global nitrogen budget

To: I suggest that the authors look into details of this flux, explaining why some regions have an enhanced C-export whereas others reveal higher DOC concentrations within the upper layers. How large must DOC and POCs concentrations be to enhance export flux of the "additional" DOC?

REPLY: This is a great suggestion that we highly appreciate. We will calculate thresholds for both small and large POC with regard to particle export, and critical values of DOC to POC formation, then add these values to the results section of our revised paper as well as identify the regions in which the thresholds are reached. We will also add a discussion exploring why the thresholds are reached in the regions in which they appear.

To: I also think that the additional carbon uptake should be traced by an increase in the C:N ratio of exported particulate matter. This can possibly be achieved even when primary production is assumed to maintain a constant C:N:P stoichiometry.

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REPLY: This is not possible due to constant model C:N ratios, see also comment about misleading use of the term 'extra carbon' above.

To: A sensitivity analysis of the pathways of excessive DOC production should also consider differences in global NPP. At which NPP (e.g. changing maximum growth rates) does the model switch from an overall positive feedback to a negative feedback?

REPLY: This is an interesting point, which could perhaps be explored in further studies. However, we do not see how this could be linked to our current ocean acidification study in a meaningful way.

To: Finally, I strongly recommend to compute the nitrogen budgets (combining NO₃ , NH₄ with the organic carbon mass converted to nitrogen with the assumed elemental ratio of 122:16) and control mass conservation of the global nitrogen budget.

REPLY: We computed the nitrogen budgets as specified, to be a stable average value of 31.1 $\mu\text{mol/l}$ for all experiments.

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