Biogeosciences Discuss., 4, S2672–S2682, 2008
www.biogeosciences-discuss.net/4/S2672/2008/

Biogeosciences Discussions

Interactive comment on "Build-up and decline of organic matter during PeECE III" *by* K. G. Schulz et al.

K. G. Schulz et al.

Received and published: 25 February 2008

General comments and suggestions:

Most general comments such as on the interpretation of the ammonium data and on the ratios of particulate organic matter collected in the sediment traps were also raised by referee 2. We believe that we have dealt with them appropriately (see our responses to the comments of referee 2 and below).

Specific comments:

1 Several times throughout the paper you refer to deep-waters.

Response We have adopted the referees' suggestion and now refer to the water below the halocline as the "deep layer water".

2 P.1, l.8: Include some data in the abstract and consider tempering the tone of the conclusions....

Response Done.

3 P.4, l.11: this sample nomenclature is the opposite way around...

Response We have corrected that mistake

4 P.5, l. 8-12: What were the nutrient concentrations prior to the addition of nitrate and phosphate. It is unclear why some of the nutrients should have been lost to deep-waters during mixing of mesocosms 1-4 only.

Response With the exception of silicate, nutrient concentrations prior to addition were close to detection limits. The nutrients were added by means of a reverse sampling with the 5m long sampling tube (additionally, the sampling procedure is now described in more detail). This means that initially we had nutrients uniformly distributed within the upper 5m of the mesocosm when the 800l of freshwater, sitting on top of the water column, were started getting mixed into depth by the aquarium pumps. In some mesocosm, the aquarium pumps did not operate at maximum efficiency and the mixing took longer that in others (for example, in M2 the freshwater was not yet mixed into depth to full extend on day t_0). If we would have added the nutrients together with the 800l of freshwater instead of the reverse sampling approach, we wouldn't have lost some of the nutrients to the deeper layer in some mesocosms.

5 P.5, l.12-18: According to the method section, mesocosms 1-3 were aerated at 350

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μatm. In the sentence starting on line 15 you state that the addition.... Are these not the target values of mesocosms 4-9?

Response We have corrected this mistake.

6 P.5, l. 20: Please specify what t_0 equates to, is this after nutrient and CO_2, equilibrium was established in all mesocosms (i.e. day 2) or is it literally day 0?

Response Day t_0 is the first day of sampling. Nutrients were added on day t_{-1}.

7 P.5, l.20: The text needs clarifying with regard to the daily sampling procedure. If the tube dimensions are 5m long and 6cm diameter then this would have a volume of 14.1 litres. Given this where does the 20 L per mesocosm per day number come from?

Response We have clarified our sampling procedures and corrected the reported numbers. 25 L per mesocosm per day translates into 2 samplings per mesocosm. We have also included additional information on the sampling of the deeper layer and the sediment traps.

8 P.6, l. 4: Please specify how much water was sampled for the various nutrient measurements....

Response We have adopted the referees suggestions and now report the amount of water sampled and the amount of replicate measurements. Furthermore, we have re-worded the whole paragraph.

9 P.6, l. 12: Change to "The supernatant was passed..."

Response Done.

10 P.6, l.25: Include information on the number of replicates analysed... and include information on whether you used an internal standard to constrain the accuracy of the

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analytical procedure..

Response There were no replicate measurements of the various particulate organic matter parameters for each mesocosm and day. The standard used was acetanilide. But how could this weighed standard be used to constrain the accuracy of the elemental analyzer?

11 P.6, l.26-27: At the beginning of section 2.2 you state that all measurements followed standard procedures. Given this statement can you provide a reference for the removal of inorganic carbon with concentrated HCl.

Response This method was developed by fuming replicate samples with concentrated HCl for different amounts of time. Over-night fuming in this particular fuming device has been determined to be sufficient to remove all particulate inorganic carbon (PIC) present. Moreover, the PIC standing stocks determined with this method compare extremely well with estimates derived from changes in total alkalinity.

12 P.7, l.1-2: Does this mean the particulate measurements were performed from the water in the sediment trap tubes?... Your methods for sampling the particulate and dissolved phases from the deep layer are very unclear.

Response We have clarified our sampling procedures. Unfortunately, we do not have any measurements on dissolved inorganic matter in the deeper layer. We did not use any preservative in the sediment traps.

13 P.7, l.11-14: The fact that you had an aquarium pump constantly mixing the upper-layer of the mesocosm is very concerning. The process of particle formation and aggregation are extremely sensitive to small-scale hydrodynamic processes, and I imagine that the pump continually acted disaggregate particles back to suspended material and prevent them from sinking... Please comment on how this pump may have affected the community composition of the phytoplankton assemblage.

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Response The paddle of the aquarium pumps was big enough to allow even bigger zooplankton to pass. We cannot rule out that particle formation and aggregation was reduced by the operation of the aquarium pumps. However, this does not influence our interpretation on the treatment specific differences.

14 P.7, l.10-15: I would also be sceptical about the element ratios obtained from the flux data for two reasons: i) over-and under trapping is caused by the hydrodynamic flow regime... that leads to some form of particle sorting based on type. ii) if particles have been re-suspended from the bottom of the mesocosm bag then it is difficult to resolve the measurements temporally. You should be able to present export measurements by adopting a budgeting approach using all of your other observations.

Response We have included a more detailed discussion on the problems associated with the sediment trap sampling. Unfortunately we do not have any measurements on the dissolved organic material in the deeper layer of the mesocosms. Hence, even if we would ignore the severe over-sampling of the sediment traps, a complete element budget would be impossible. Because of the problems associated with the sediment traps and the missing dissolved organic matter data at depth, the element ratios measured in the sediment traps cannot confirm our interpretation of enhanced organic carbon export and remineralization under elevated CO_2 conditions. However, they do not contradict our conclusions, either (which is based on two independent observations).

15 P.8, l.26-27: Presumably you are talking about ammonium concentrations here... The end of the sentence is clumsily worded.

Response We have made the necessary modifications.

16 P.9, l.29: The metazooplankton biomass will increase in part due to the exclusion of natural predators, from the mesocosm experiments, please mention this.

Response Done.

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17 P.11, l.16: Export numbers could have been constrained with an elemental budgeting approach with correct sampling of both layers. If the relevant measurements of both water masses were made this should be included. If the measurements were not made this needs to be identified as an experimental short-coming and recommendations for future sampling protocols discussed.

Response Unfortunately, there were no DOM measurements in the deeper layer of the mesocosms. We have included some recommendations for future mesocosm studies.

18 P. 11, l.24-25: Please avoid phrases like seemingly and appeared when discussing data.

Response We have rephrased the respective sentences and included some proper statistics.

19 P. 12, l.1: By using the phrase on the other hand you are implying that this observation is different to the one presented in the previous sentence.

Response Yes it is to some extent, as shown by the statistical calculations.

20 P.12, l:21-23: Is there any evidence in the literature that ammonium regeneration is oxygen-dependent in the water column? I do not think it is appropriate to provide a sedimentary reference here.

Response With regard to oxygen-dependency, we have not found anything on ammonium regeneration in the water column. However, as discussed now in more detail, the two ammonium measurements in the deeper layers of the mesocosms are probably highly impacted by the processes occurring in the sediment accumulating on the bottom of the mesocosms.

21 P.12, l.23: You have not presented oxygen concentrations for the deep-layer. You

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are making a big assumption about oxygen based on your ammonium data. You have also ignored the process of photorespiration to explain your ammonium data.

Response We have completely restructured the discussion on the possible deep layer oxygen concentrations. We show that the differences in ammonium concentrations observed in the upper surface water originate from deeper layers, thus excluding photorespiration as the main driver. Our assumptions are now based on two independent observations: treatment specific differences in organic carbon export to depth and surface water oxygen concentrations at the end of the experiment.

22 P.13, l.1-3: According to table 1 TEP measurements were made on the samples. Why is this data not presented here?

Response Given the high background concentrations of TEP and uncertainties in the analytical measurements, the TEP data would not pick up the relatively small differences which we would expect to observe. Furthermore, TEP was measured in terms of Xanthan– equivalents which, for comparison, would need to be transformed into carbon units. Unfortunately, the carbon content of TEP under the different CO_2 conditions was not determined.

23 P.13, l.1-3: As mentioned previously, do you think that the conditions in the mesocosm bags and the presence of aquarium pumps are representative of particle dynamics? ...If the export measurements were mediated by enhanced TEP formation then the experiment is of limited use in considering how these mechanisms might operate in a natural environment. Please comment.

Response As stated above, the aquarium pumps were operating in all mesocosms. Hence, the processes observed (such as higher dissolved inorganic carbon draw-down at elevated CO_2 and higher loss of this carbon to the deeper layer) cannot be caused by the aquarium pumps. We agree, that the aquarium pumps add a certain element of uncertainty to whether the strength (not the differences between treatments) of the

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export observed in our mesocosms could be translated to the open ocean. However, our main conclusions are not based on absolute amounts.

24 P.13, l.1-3: I thought the conclusion of Engel 2002 was that a further increase in atmospheric CO_2 would not lead to a higher rate of DIC to TEP conversion, since the rate of exopolymer carbohydrate production seems to be already at its maximum.

Response It seems that the conclusion of saturated DIC to TEP conversion under elevated CO_2 of Engel et al. (2002) is based on the observation that phytoplankton CO_2 uptake is saturated at ambient seawater CO_2 conditions. This in turn, was based on the assumption that phytoplankton relies on diffusive CO_2 uptake which, as we know now, is not the case.

25 P.13, l.11: As discussed above, ammonium in your mesocosms is probably mediated by photorespiration.

Response We have included the possible contribution of photorespiration to the observed ammonium concentrations in the discussion of our manuscript.

26 P.14, l.24-27: If this explanation is correct you would expect that the 3x treatment showed the largest deviation away from Redfield values. According to Figure 10d on day 22 the DOC/DON numbers for the 3x experiment were the highest and closest to Redfield. Do you have DOC:DON measurements prior to day 9?

Response As indicated by the relatively high standard deviations, all data on dissolved organic matter (and their respective ratios) have a relatively high measurement error. Hence, we wouldn't like to draw conclusions on treatment specific differences in respective element ratios. There is no meaningful data on DOC/DON prior to day 9.

27 P.14, l.9-11: It seems rather unlikely that the proposed mechanisms of reduced organic nitrogen remineralization and increased organic carbon remineralization at el-

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evated CO_2 would act to cancel each other out and result in constant sedimentary POC/PON values.

Response We have completely restructured the discussion on organic nitrogen remineralization and addressed the problems associated with the sediment trap sampling (see above).

28 P.15, l.1-2: I would question points 2 and 3 based on some of the comments made above.

Response We have presented further evidence for the scenario of enhanced oxygen depletion in the deeper layer of the 3x CO_2 mesocosms and provided a better reasoning for the ammonium regeneration hypothesis.

Technical corrections:

1 P.1, l.4: Delete subsequent decreasing and replace with consequent decrease in

Response We have replace subsequent with consequent

2 P.1, l.8: Change mixed surface waters to upper layer of mesocosm.

Response Done.

3 P.2, l.17 / P.2, l.26 / P.3, l.12: Change 21 to 21st.

Response Done.

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4 P.2., l.18: Change climate relevant to climatically active.

Response Done.

5 P.5, l.10: Change to deep-layer.

Response Done.

6 P.6, l.9: Insert immediately between which and were.

Response Done.

7 P.6, l.11: Try to avoid starting sentences with then.

Response Done.

8 P.6, l.18: Delete prevent and replace with minimise the effect of

Response Done.

9 P.6, l.26: Delete Before and replace with prior to

Response Done.

10 P.7, l.11: Insert layer after deep.

Response Done.

11 P.12, l.8: Delete could be caused by and replace with indicates that.

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Response Done.

12 P.12, l.9: Delete which. At the end of the sentence add over the range examined in this study.

Response Done. The information about the CO_2 range is given in the next sentence.

13 P.12, l.17: Change to deeper-layer.

Response Done.

14 P.13., l.24: This should be section 4.2

Response We have corrected this typo.

Interactive comment on Biogeosciences Discuss., 4, 4539, 2007.