Interactive comment on "The role of polysaccharides and diatom exudates in the redox cycling of Fe and the photoproduction of hydrogen peroxide in coastal seawaters" *by* S. Steigenberger et al.

S. Steigenberger et al.

ss2p07@noc.soton.ac.uk

Received and published: 26 November 2009

Firstly thanks to the Referee for the time spent with this and the useful comments on the manuscript. You will find our reply to the comments below.

Anonymous Referee #2 Received and published: 29 October 2009 General Comments This paper investigates and important current research issue viz. identifying potential sources of dissolved organic matter in seawater which can photosensitise the formation of superoxide anion and hence its disproportionation into hydrogen peroxide, and

then the effect this production of hydrogen peroxide has on the redox cycling of iron. A series of carefully controlled experiments are undertaken using both artificial and natural polysaccharide material and then a mathematical model is set up to simulate the observed experimental results. The main conclusion that UV-irradiation of seawater containing high concentrations of exudates increased the steady-state concentrations of Fe(II) via the production of H2O2 seems fully justified from the experimental results. The suggestions for future work also seemed well justified in terms of the present results Specific Comments Although definitive results were obtained in terms of peroxide production rates in relation to extent of cycling between the Fe(II) and Fe(III) oxidation states, I did not find the text and associated figures particularly easy to read in order to clearly establish what these results were and the conclusions that followed from them. The present model appeared to follow that of the models developed by Weber et al. (2007), Meunier et al (2005), and Rose & Waite (2003c) but was also not easy to follow as described in this paper - the list of chemical equations and kinetic parameters given in Table 1 was not easy to connect together into an overall picture of the model. More detail should be provided on the basis of the model and, to this end, at least one flow diagram summarising (including relevant rate constant expressions) the various processes for which rate constants were input into the model would be helpful (e.g. see Fig. 3 of Weber et al. 2007) p.7797 l 20-21 How sure can you can you be that you reached a global maximum ?

Reply: We reworded this sentence in the MS to make clear that the global minimum (!) was found.

p7798 l10-15 This explanation for the observation of detectable levels of H2O2 in pure MQ seems very unlikely.

Reply: Since our MQ system did not have a UV unit to oxidize DOM and the Tedlar sample bags were carefully rinsed with MQ prior to use, this explanation seems highly probable.

l 20 – 23 although you discuss the main chemical structural differences between the molecules of the three PS , surely the most important feature is their differences in absorbances at wavelengths < 300 nm ?

Reply: Thank you for pointing this out. This is surely true and we agree to refer to this fact already at this early point in the MS not just in the Results section and we have included this into the text.

p.7800 l17-19 Why didn't you try to lower the initial H_2O_2 concentrations ? I really don't understand why organic free seawater (UVSW) should have a 50 fold higher initial concentration of H_2O_2 than a natural SW sample.

Reply: H_2O_2 was formed during the photooxidative removal of DOM from the natural seawater in order to form the organic free seawater (UVSW). To make the initial conditions of all treatments in SW and UVSW as similar as possible we lowered the H_2O_2 concentration in the UVSW.

p.7801 l 6-7 how closely do the conditions under which the published values (Croot et al etc.) were measured , equate to the present ones ?

Reply: The main point is that our rates are consistent with both, existing lab (Millero et al.) and ocean field measurements (Croot and Laan, Kuma et al.). Details to compare with our results can be found in these papers.

l 10 how do you know the decay follows an exponential decrease and not some other mathematical function ?

Reply: All previous work on Fe(II) oxidation demonstrates a 1st order decay and this describes our data nicely. To us there seems to be no reason for any far-fetched speculation.

l 26-27 rather than' exudates ...photochemically produce H_2O_2', I would prefer the wording 'exudates ..... photosensitise the production of H_2O_2 '

Reply: We agree with the referee that this statement is not completely justified and we have reworded this sentence.

p.7802 l1 As noted earlier, Table 1 is a list of equations and their rate constants which hardly, if at all, shows part of the iron cycl,. Include these equations in a diagram with interconnecting arrows etc. to better illustrate the model (see Fig. 3 of Weber et al. 2007) Reply: We inserted a graphical representation of the model structure in the manuscript.

l 5-6 How justified are you in making this assumption that stabilisation of Fe(II) is a photoreductive process ?

Reply: However, the presence of exudates leads to the net reduction of Fe(III) to Fe(II) most likely via photoinduced processes, because experiment 2 did not show a stabilizing effect of PS in the dark.

l14 What determined your choice of these starting concentrations ?

Reply: These values reflect the experimental conditions for the major species considered in the model; the initial concentration of short-lived species such as superoxide do not influence the model outcome very strongly and were chosen here reflecting our ignorance.

l 17 Would you expect your fitted value for kCDOM to be different for natural irradiation of other types of natural CDOM compared the value you derive from your artificial irradiation of the PS compounds ? If so, then how generally applicable is your model to CDOM in all coastal seawaters ? ?

Reply: Whilst the referee raises an important and interesting point we could only speculate about this and we believe that this is beyond the scope of the current MS.

l 28 Your modelled initial non-linear increase in the accumulation of H_2O_2 is surely not in agreement with experimental observations ?

Reply: In this experiment we only measured the hydrogen peroxide concentration at the beginning and at the end. The model provides a good fit to the measured data and it is not obvious to us why in this case (presence of Fe(II)) one should expect a linear increase of H2O2.

p.7803 Paragraph 1 – all of these verbal explanations for the effects of variations in modelled parameters are difficult to follow without a visual representation of the basic model.

Reply: We inserted a graphical representation of the model structure in the manuscript.

p.7804 l12 these rate constants for formation of superoxide seem VERY small – are they correct as written here ?

Reply: They are actually not particularly small. Maybe the reviewer did not notice that the units were M sˆ-1, not nM sˆ-1. This corresponds to production of 1 nM of superoxide in a time-span between 15 and 100 seconds.

L 19 How minor was the effect of EDTA ? You should quantify this.

Reply: This quantification had already been included into the text see lines 23 – 29.

p.7805 l10 'redox state of iron' rather than 'iron speciation' ?

Reply: We changed this in the text.

l20-21 I suspect only a small fraction of the total coastal CDOM could possibly be attributed to diatom exudates and therefore you are not justified in making this claim.

Reply: Considering the substantial contribution of polysaccharidic material to coastal water DOM (Guo et al. 2009, Mannino and Harvey 2000,...) we believe that this conclusion is justified.

L 23 '..effect of H2O2 induced Fe(II) oxidation ....

Reply: We realized that this expression was confusing and changed this sentence.

L24 particle size for what ? CDOM ? make this clear.

Reply: We reworded this sentence.

p.7817 Fig 4 why continue the traces past 1000 s when there is no longer any measurable Fe(II) after this time ?

Reply: We plotted this time series in the same way as the other diagram of this experiment (Fig. 3) and do not think this will cause confusion.

p.7818 In the trace in this Fig 5, how can you report Fe (II) concentrations below the detection limit of your analytical technique ?

Reply: As the referee will know the detection limit is an operationally defined value (3*σ). We realized that this had not been made clear. We included this information into the method section. A slight scatter of the data points around the detection limit does not affect the main point of this figure, i.e. the significantly higher Fe(II) values in the sample containing algal exudates than in the sample without exudates.

Technical Corrections In the title, I am not sure how justified inclusion of 'coastal' to describe the seawater is justified given the nature of the experiments that were subsequently undertaken.

Reply: Since the seawater we used for our experiments was collected at a coastal site, since the diatom culture we harvested the exudates from was grown under high nutrient conditions and since the Fe concentrations range up to 100 nM, we believe that the use of the word 'coastal' is justified and describes the experimental conditions best.

p7790 l 9 ..in the presence of...

Reply: This has been changed in the text.

l 13 ..seem to have the potential to play

Reply: This has been changed in the text.

p7795 l15 where did these limits of detection come from ? Why 'about ' ?

Reply: See earlier comment about the detection limit.

l 27 similarly where did this detection limit come from ?

Reply: We included the information how the detection limit had been calculated into the text.

p7796 l 9, l15 Again ehere did this limit of detection and standard error come from ? Did the authors determine all of these values themselves or just rely on the orginal publications for the methods – if so their sources all need to be referenced.

Reply: We included the information how the detection limit had been calculated into the text.

L24 use of activated charcoal to remove H2O2 needs to be referenced.

Reply: The use of activated charcoal was not based on published literature, but showed the desired effect without contaminating the sample with Fe as described in the text.

p7797 l 6 ..a variable order integration

Reply: This has been changed in the text.

l 15 Nelder-Meade simplex algorithm needs referencing

Reply: This reference has been included into the text.

p.7800 l1-2 Surely prior removal of organic matter would lead to low not high H2O2 concentrations ?

Reply: The (photooxidative) removal process of DOM generates the high H2O2 concentrations in the organic free seawater in the first place.

p.7803 l23-24 Messages cannot be drawn from anything – unscientific English – reword

Reply: This has been changed in the text.

p.7804 l.5 'by the via light"' ???

Reply: This has been changed in the text.

l.20-21 lower than the concentrations observed ..

Reply: This has been changed in the text.

p.7817 in legend for Fig 4 , ..with PS added (open circles).

Reply: This has been included into the legend.

p.7819 last line of legend - ..in steady-state Fe (II) concentration

Reply: This has been changed in the text.

———————————————————————

Interactive comment on Biogeosciences Discuss., 6, 7789, 2009.