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Comment

***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.**

Anonymous Referee #2

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General Comments

This paper investigates an 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

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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 | 20-21 How sure can you be that you reached a global maximum ?

p7798 | 10-15 This explanation for the observation of detectable levels of H₂O₂ in pure MQ seems very unlikely.

I 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 ?

p.7800 | 17-19 Why didn't you try to lower the *initial* H₂O₂ concentrations ? I really don't understand why organic free seawater (UVSW) should have a 50 fold **higher** initial

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concentration of H_2O_2 than a natural SW sample.

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

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

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

p.7802 |1 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)

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

I14 What determined your choice of these starting concentrations ?

I 17 Would you expect your fitted value for k_{CDOM} 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 ? ?

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

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.

P.7804 |12 these rate constants for formation of superoxide seem VERY small – are they correct as written here ?

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

p.7805 I10 'redox state of iron' rather than 'iron speciation' ?

I20-21 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.

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

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

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

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

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.

p7790 I 9 ..in **the** presence of...

I 13 ..seem to **have the potential to** play

p7795 I15 where did these limits of detection come from ? Why 'about ' ?

I 27 similarly where did this detection limit come from ?

p7796 I 9, I15 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 original publications for the methods – if so their sources all need to be referenced.

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

p7797 I 6 ..a variable **order** integration

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I 15 Nelder-Meade simplex algorithm needs referencing

p.7800 I1-2 Surely prior removal of organic matter would lead to low not high H_2O_2 concentrations ?

p.7803 I23-24 Messages cannot be drawn from anything – unscientific English – reword.

p.7804 I.5 'by the via light,,' ???

I.20-21 lower than **the concentrations** observed ..

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

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

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