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Biogeosciences Discussions

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

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

Anonymous Referee #1 Received and published: 22 September 2009 Part 1. General comments: The following is my review of "The role of polysaccharides and diatom exudates in the redox cycling of Fe and the photoproduction of hydrogen peroxide in coastal seawaters" by Steigenberger et al.. The manuscript presents significant new

and novel information regarding the effect of artificial acidic polysaccharides (PS) and exudates of Phaeodactylum tricornutum on the half-life of Fe(II) and production of hydrogen peroxide. The manuscript includes a model describing the photochemical redox cycle of iron incorporating peroxide which is somewhat supported by the observed data. The authors' main conclusion is that diatom exudates could play an important role in the photochemistry of iron and peroxide in coastal waters. The data presented is original and should be of interest to a broad spectrum of aquatic scientists interested in the cycling and speciation of trace metals such as iron. The manuscript is well written, organized with an appropriate number of figures and tables. I would suggest that it be published once the authors have addressed some of my concerns discussed below. Part 2. Specific comments: 1. The authors suggest in the beginning of the results section that "The H2O2 concentration in all samples increased linearly during the experiment, when the samples were illuminated." I do not entirely agree with this assertion because during the first three data points in Fig. 1 for all four treatments there is little or no change in peroxide concentration with irradiation time. I would suggest that the statement regarding peroxide photoproduction be modified to acknowledge this pattern in the data. Also how were production rates calculated given the relatively constant peroxide concentrations during the first three data points?

Reply: Considering the sdev and the high r2 values of 0.97-0.99 for a linear fit to the hydrogen peroxide concentrations it seems reasonable to believe that a linear pattern as previously described (Cooper et al., 1988; Miller et al., 1995) is also valid in our study and we calculated the H2O2 formation rates accordingly as the slope of a straight line fitted to the data points and forced through the respective initial value of each of the five samples. This information has been incorporated into the text and we thank the reviewer for pointing this out to us

2. I am a little concerned about the relatively high production of peroxide in MQ water presented in Fig. 1. The authors suggest that "The H2O2 formation during illumination of the MQ water was probably due to organic matter leaching from the resin cartridge

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of the MQ system." The authors need to acknowledge this and not call the MQ water organic free as it probably is not. Another consideration is that the organics in the MQ water could enhance production of peroxide in the irradiated polysaccharides samples by some secondary photo process that would not occur in natural samples. Also they could be directly involved in the photochemical transformations involving Fe.

Reply: We used MQ water as a low organic comparator. For all the following illumination experiments which contained Fe we used only UV photooxidised seawater not MQ water and the results were not affected by potential organics in the MQ water. We appreciate the reviewer's point but feel that the text currently there makes clear what is happening.

3. The data presented in figure 5 need some explaining. The authors suggest that "In the UVSW without exudates the Fe(II) concentration continued decreasing exponentially reaching the detection limit after 20min" How can the authors quantify Fe(II) concentrations below the detection limit as reported in Fig 5? Also the authors report that "The detection limit of this method is about 8 nmol L-1 of Fe(II)" They need a reference or data to back up this claim as most often the detection limit for the ferrozine analysis is reported closer to 20 nM for this path length cell.

Reply: The shown data points >20 min in Fig. 5 encompass (apart from 2 values) the detection limit in their sdev . We do not intend to challenge the detection limit of the ferrozine method, since we are anyway working with artificially high dissolved Fe concentrations. But what is obvious is that Fe(II) concentrations in the sample containing algal exudates are significantly higher than the detection limit. Regarding the detection limit of the ferrozine method, we calculated the LOD of 8 nM as 3x sdev of the 50 nM Fe std. addition signal. Thanks to the reviewer we realised that this information was missing and included it into the method description.

4. In the discussion of the effect of diatom exudates and UVA/B radiation on the oxidation of Fe(II) in seawater the authors state that "As we have found no stabilizing effect of

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polysaccharides on Fe(II) concentrations in the dark, we assume that the stabilization of Fe(II) is due to a photoreductive process. Photoreduction can occur both directly, presumably as photoreduction of Fe(III) (reaction1 in Table 1) bound to some organic ligand contained in the exudates, and indirectly via a reaction of Fe(III) with superoxide". It would be very useful to present the Fe(III) data as well as the Fe(II) in order to evaluate the mechanisms involved in the photo mediated cycling of Fe in this system.

Reply: We strongly agree with the referee, but due to logistical constraints we were only able to monitor the dissolved Fe(II) throughout the experiment. However, measurements of total dissolved Fe at the beginning and end were very similar indicating no major loss of Fe from the system.

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