Biogeosciences Discuss., 6, C2113–C2115, 2009
www.biogeosciences-discuss.net/6/C2113/2009/

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.

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?

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 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.

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.

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 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.

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