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Biogeosciences Discussions

Interactive comment on "Dissolved iron (II) in the Baltic Sea surface water and implications for cyanobacterial bloom development" *by* E. Breitbarth et al.

Anonymous Referee #1

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Referee report for:

Journal: Biogeosciences Title: Dissolved iron(II) in the Baltic Sea surface water and implications for cyanobacterial bloom development Author(s): E Breitbarth et al. MS No.: bg-2009-39 Special Issue: Iron biogeochemistry across marine systems at changing times

It is an interesting article combining several difficult and complex techniques to determine the biogeochemistry of Fe in a complex environment as the Baltic Sea to deduce its importance for cyanobacterial bloom development. Because the subject is complex and the measurements are difficult the authors should be very careful in their presenta-

tion of the results and the conclusions that they draw based on their data. Furthermore, to give the reader trust in their results they should be more precise in their description of the methods they used. Readers should also be carefully guided in the interpretation of the data leading to the proposed conclusions. Combining results and discussion in a structural way may improve the clarity of the manuscript.

At this moment the manuscript still contains too many statements that are important but not properly proven and discussed in relation to available knowledge/literature or their own data. Furthermore, alternative explanations for a number of observations are not discussed.

Abstract:

1) p3804, line 8: Indication for organic Fe(II) complexation resulting in prolonged residence times in oxygenated water was observed.

The authors have to be very careful with this statement. One can find this suggestion more and more in the literature. It is suggested due to lack of other explanations for persisting Fe(II) concentrations during nightime or unexpected slow oxidation kinetics. And most probably there may indeed be Fe(II) complexing ligands present in the seawater. However as far as I know nobody indefinitely showed/published their presence as being significant and nobody showed indefinitely in the literature that Fe(II) complexed to natural occurring Fe(II)-binding ligands can actually be detected using FIA. Especially as FIA depends on the oxidation of Fe(II) in the flow cell which means that the Fe(II) should be released by the Fe(II)-binding ligand at that pH and oxidized at a time-scale that the sample is in the flow cell in order to be measured. By repeating this suggesting without care suggestions become automatically facts over time. In my opinion, this suggestion needs careful discussion in the manuscript.

1 Introduction:

Paragraph 1.2 The Baltic Sea, cyanobacterial blooms, and iron

2) p3807, line 2: Since Fe(II) is unspecifically available to all phytoplankton

Is there a reference for this statement?

2 Methods:

Paragraph 2.2 Seawater sampling and processing

3) P3809, line 9: which brand and type of 0.2 um polycarbonate membranes?

How were the DFe samples acidified?

How were the samples for organic complexation stored? How long were they stored before measurement?

4) p3809, line 16: Fe(II) concentrations were determined within the shortest time possible, usually within four minutes after sampling for oxygenated surface water and a maximum of one hour after sampling for anoxic deep water.

Do the authors suspect a significant loss in Fe(II) with four minutes between sampling and measurement of the oxygenated seawater samples? Especially as the authors estimate Fe(II) half life times between 1.1 and 15.2 minutes in oxygenated seawater? The same question can be asked for the anoxic samples. The authors report estimated Fe(II) half life times between 7.6 and 350.2 minutes and a sampling time of an hour. Did the authors compensate the final values for differences in Fe(II) oxidation rates and the time between sampling and measurement? If yes, how did they do that?

Furthermore, did the anoxic samples stay anoxic during this hour? Wouldn't filtration of the anoxic sample through a 0.45 um PVDF membrane introduce oxygen in the samples affecting oxidation rates leading to an underestimation of the Fe(II) values?

Paragraph 2.3 Fe(II) analysis

5) Which brand of luminol did the authors use? Was there any pre treatment of the luminol, e.g. overnight stabilisation, before use?

6) The description of the Fe(II) analysis lacks information on the standard additions. Where the standard additions linear? Did the authors compensate the signal of the standard additions for Fe(II) oxidation after addition of the standard to the standard addition matrix? Especially in the Baltic Sea with its changing environment with respect to salinity, pH, and oxygen it is important that the standard additions are performed in a similar seawater matrix as the samples. What did the authors use as standard addition matrix? As the oxidation of Fe(II) by O2 in the flow cell leads to oxidation of luminol and subsequent luminescence how would anoxic conditions affect the measurements? Did the authors do standard additions with anoxic water? If yes, how did they keep the standard additions anoxic?

7) Do the authors have any information on the analytical performance of their Fe(II) analyses that they could include in the manuscript?

Paragraph 2.5 Deck incubations

8) What was the ambient seawater temperature?

9) How much time was there between getting the quartz incubation bottle from the incubator and the measurement of Fe(II)? Did the authors transport the bottle in the light or in the dark? Did they filtrate the samples before analysis? How would all this treatments affect the final Fe(II) concentrations?

Paragraph 2.6 Organic Fe(III) complexation

10) The samples were frozen and kept at which temperature?

11) What was the salinity of the samples? Were the salinities so low that it may affect the log K of TAC as shown by (Gerringa et al., 2007)? If yes, how would that affect the results?

12) Did the authors use a 0.01M TAC stock solution and a final concentration of 10 uM TAC in their titration samples? This is not clear from their method description.

13) Please include a reference for the inorganic side reaction coefficient.

Paragraph 2.7 DGT methodology

14) p3812, line 12: every five . . .. . .what?

15) DGT units were deployed at depths between 0.5 and 120 m. What were the salinities at these depths? How would a difference in these salinities affect the final outcome, e.g. (Yezek et al., 2008)?

16) p3812, line 22: Gels were eluted with 5 ml 5 M HNO3 (quartz distilled). . ..

Which brand and quality of HNO3, how often quartz distilled?

17) p3812, line 25: Prior to analysis, water samples were diluted 4-fold with 0.16 M HNO3 (Merck suprapur) in MilliQ water.

First the authors use quartz distilled HNO3 to elute the gels and subsequently they use HNO3 of Merck suprapur to dilute water sampes 4-fold before measurement? Is Merck Suprapur HNO3 clean enough for these levels of Fe?

Could the authors report how DGT blanks compare with the labile Fe values of the DGT samples?

3 Results

Paragraph 3.2 General meteorology

18) p3816, line 20: Of particular interest with regard to water column mixing, H2O2 and Fe(II) production, and rainwater input is the week directly before the sampling events.

The text doesn't make clear why the week directly before the sampling is of particular interest?

19) p3816, line 24: As time and timescales are important when investigating a fast process as the Fe redox cycle and the authors suggest in the abstract that rainwater is important for the provision of Fe(II), could they indicate how long prior to sampling on

4 July at LD significant rain deposition was recorded?

3.3 Fe(II)

Paragraph 3.3.1 Fe(II) in the oxygenated water layer

20) p3817, line 11: On most occasions, Fe(II) concentrations are elevated in the upper meters of the water column and decrease proportionally with depth (LD 1 August, GD 20 June, 2 and 14 August; Figs. 3f, 4f, 5e, f).

Elevated surface Fe(II) concentration would suggest photoreduction. If the authors write proportionally with depth could they relate this proportionality to irradiance using the Beer-Lambert law? Are there any light attenuation coefficients published for similar Baltic water masses that could be used? Can you relate secchi depths to attenuation coefficients?

21) p3817, line 12: At 5m depth, chl-a increases from 1.6 to 4.1 μg L$-$1 over the course of the summer and Fe(II) shows a maximum of 0.64 nmol L$-$1 on 2 August (Fig. 6a).

I am not sure why the authors included this sentence especially on this location in a paragraph that deals with Fe(II) without any direct connection to their Fe(II) results?

22) p3817, line 15-onwards:

First the authors mention oxidation rate calculations in values for half life times attributed to pH at GD of 0.04 -0.32 min-1 and 1.00-1.03 min-1 at LD. Then they mention that O2 is the main factor in oxidation because half lives based on H2O2 are longer?

This information is a bit confusing. Maybe it should be explained better how oxidation rates were calculated and which assumptions were used.

23) p3817, line 22-onwards:

The authors sum here rain events which, if the results and discussion are separated, should be mentioned under the meteorological data. Rain events are not connected

here to the Fe(II) concentrations. In contrary, the authors continue the text with Fe(II) concentrations of which they show are not related to rain. . ..this gets confusing. Furthermore, how long were the rain events before Fe(II) sampling? Considering the very short half lives of Fe(II), how sure can the authors be that measured Fe(II) concentrations are a result of rainfall as suggested in the abstract?

24) p3818, Line 1:

I find it hard to distinguish a clear signal in temperature, salinity and phosphate. Do the authors find this difference in water masses back in a temperature-salinity plot?

25) p3818, Line 5-onwards:

The authors mention enhanced Fe(II) concentrations at depth together with low oxygen concentrations. Could interference of reduced Vanadium with their measurements play a role in the Baltic Sea (see (Hopkinson and Barbeau, 2007))?

Paragraph 3.6 Total and dissolved iron concentrations and organic iron(III) complexation at 5 m depth

26) p3820, Line 22: causing the surface seawater to be deficient of organic iron ligands from 20 June on.

I assume that the authors talk here about free Fe-binding ligands?

27) Figure 7b:

Why do the authors show negative concentrations of excess Fe-binding ligands in figure 7? If negative there are per definition no free Fe-binding ligands.

28) p3820, Line 26-28:

If the authors don't have any free Fe-binding ligands (excess Fe-binding ligands), there was probably no curvature in the titrations? If there was no curvature in the titrations how was the log K of the natural occurring Fe-binding ligands determined? This is

unclear to me? How do the titrations look like? Maybe the authors can show some in a figure to give readers an idea of the quality of the titrations?

29) p3821, line 1: The trend in Fe' anti-correlates the excess ligand concentrations (Fig. 7b).

If the term "anti-correlates" is used, there need to be statistical information to show if the (anti-) correlation is significant.

Paragraph 3.7 DGT data

30) The authors find a visually similar pattern between Fe(II) and DGT labile Fe. However, is there a direct connection between Fe(II) and DGT labile Fe? How does DFe relate to Fe(II) and DGT labile Fe along this depth profile? Could it not be that DFe in general determine the amount of DGT labile Fe? I would like to see some data/discussion about this.

Paragraph 3.9 Deck incubation experiment – H2O2 and Fe(II) production and consumption

31) p3822, line 6: The 0.2 μm filtered seawater however increased from 699 to 3229 nmol $L-1$ during the day (Fig. 11a) and is thus considerably higher than levels detected in the depth profile at this station on the same day (Fig. 4f).

Is it possible that cell breakage occurred during filtration leading to more organic matter in the filtered fraction leading to higher H2O2 production under irradiance?

Paragraph 3.8 Macronutrients at 5 m depth

32) Nutrient ratios are reported here but not further used in the discussion?

4 Discussion

Paragraph 4.1 Main findings

33) p3823, line 3: A – The fully oxygenated euphotic zone where photoreduction of

Fe(III)-complexes and deposition by rain are the main sources of Fe(II).

This statement reads as a conclusion. However, to make this statement it would be necessary to discuss three aspects: i) Has it been shown that photoreduction occurred? Yes, the diel cycle of Fe(II) production in the incubation data suggests photoreduction. Occurance of photoreduction in the field could be investigated by the proportionality between Fe(II) and depth in relation to irradiance. ii) Fe-(III) complexes, although it has been shown with model- and suggested for in situ organic ligands that the complexed Fe is photoreducible and the ligand may be photodegraded (e.g. (Barbeau et al., 2001; Maldonado et al., 2005; Powell and Wilson-Finelli, 2003; Rijkenberg et al., 2006a)), the opposite has also been shown for model and in situ ligands (e.g. (Kunkely and Vogler, 2001; Rijkenberg et al., 2006a; Rijkenberg et al., 2006b). Fe from small Fe colloids (which may contain organic electron donors) have also shown to be involved in Fe(II) production (e.g. (Rijkenberg et al., 2006a; Wells et al., 1991)). Because, as far as I can judge, the data itself does not show any direct evidence for the photoreduction of organically complexed Fe I think this aspects need to be better discussed before used in such a statement. iii) The authors propose rain as a main source of Fe(II). It needs to be shown with the data that rain could be a main source of Fe(II). To do this the reader needs to know how much time there was between the rain event and your Fe(II) measurement. Considering the oxidation rates of the Fe(II) the authors should evaluate if it would be possible to detect any Fe(II) originating from this rain event. The authors should furthermore evaluate which proportion originates from the rain event as compared to photoreduction if they want to propose that both mechanisms form a main source of Fe(II) in the Baltic.

Paragraph 4.2 Fe(II) in the oxic-anoxic transition zone and in anoxic deep water

34) p3823, line 16: Thermodynamics favor all iron in this water layer to be reduced to Fe(II) as also suggested by Strady et al. (2008).

It is unclear here if this is a statement based directly on data or that it is taken over

from (Strady et al., 2008).

35) p3823, line 17: The Luminol chemiluminescent flow injection analysis (CL-FIA) used for the Fe(II) measurements here (Croot and Laan, 2002; Rose and Waite, 2001) apparently only detects the ferrous ions and is insensitive to iron sulfides, explaining the discrepancy between Fe(II) and total dissolved Fe measurements in anoxic deep water at the Gotland Deep station, which differ by one order of magnitude considering the total dissolved Fe data provided by Strady et al. (2008).

This statement requires a precise description of the methods used to measure Fe(II) in the anoxic deep samples. Were the samples kept anoxic, if not, how long were samples under oxic conditions and what does this means for the final Fe(II) data? Further, in what matrix were the standard additions performed to calibrate the Fe(II) signal of the anoxic deep samples? At this moment the discrepancy between Fe(II) concentrations and dissolved Fe concentrations could for the reader also be the result of short comings in the Fe(II) analysis and nothing to do with the presence of Fe sulphides.

36) p3823, line 23: Fe(II) levels detected in anoxic waters at Landsort Deep, correlate with H2S data (Fig. 3c–f), indicating the formation process of ferrous ions and hydrogen sulfides to iron sulfides 25 and further supporting the specificity of Luminol CL-FIA to ferrous ions.

The word “correlate” asks for statistical information on significance.

Paragraph 4.3 The role of organic Fe(III) complexation

37) p3824, line 20: Our data imply that especially wet deposition and photochemical reduction of organic Fe(III)-complexes are important sources of Fe(II) to the surface layer at Gotland Deep and Landsort Deep.

The data may imply the above statement but the authors did not show this yet to the reader, see also the comment above (p3823, line 3).

4.3.1 The role of organic Fe(III) complexation

38) p3824, line 24: While organically complexed dissolved iron is progressively decreasing at Gotland Deep over the course of the study (Fig. 7b), this substratum for photoreduction of iron apparently is present at sufficient levels since Fe(II) concentrations do not correlate with iron ligand concentrations.

The statement that the organic Fe(III) complexes form the substratum for the detected Fe(II) has not been shown by the data and is not properly discussed. Most probably there are additional sources for Fe(II) as e.g. colloidal Fe. This means that it can not be concluded from the data that the photoreducible Fe fraction is in excess to the actual Fe(II) produced.

39) p3825, line 3: The decrease of iron binding ligands parallels the decrease in PO4 and anti-correlates with chlorophyll−a increase at 5m water depth (Figs. 6a, 9a). Therefore, biological uptake of ligand bound iron probably is responsible for this trend in parallel to dissimilatory photoreduction of dissolved organic matter.

This statement seems to be based on visual inspection of different graphs with few data points over a relative long time scale. Some statistics resulting in significance would allow a statement that includes the careful phrase “probably” but this important conclusion (even when “probably” is included) could, in my opinion, not be based on the data as presented here.

40) p3825, line 4: Moreover, the conditional stability constant of iron binding ligands in the beginning of the study (log KFe0L=10.3, Fig. 7b) closely resembles that reported for fulvic acid isolated from river natural organic matter (log Fe0L=10.4, Rose and Waite, 2003).

If the authors investigate the literature they may find that it also resembles natural organic ligands in other oceanic regions and even model ligands. It is very difficult and probably not possible to use the log K to identify organic Fe-binding ligands. This remark also relates to further suggestions that the log K resembles marine Fe-binding ligands.

41) p3825, line 11: During the middle of the summer log KFe0L is elevated (>11.5) and approaches the strength of marine iron binding ligands (Rue and Bruland, 1995; Witter et al., 2000), but decreases again between the 2 and 14 August sampling (Fig. 7b). At the same time chlorophyll−a and iron ligand concentrations increase again. This indicates that the iron ligand characteristics are connected to the phytoplankton bloom dynamics and that at least a proportion of the ligands present may be biologically produced.

The authors may be right. However the method description and presentation of the data does not allow the reader to judge the quality of the organic Fe-complexation data. Especially how the log K’ was determined without an excess of ligands present to provide the titrations with a curvature?

Furthermore, the indication is only based on the visual observation of trends. It seems impossible to draw from such visual observations using a limited amount of data points the two important conclusions that: i) the iron ligand characteristics are connected to the phytoplankton bloom dynamics, and ii) at least a proportion of the ligands present may be biologically produced.

42) p3825, line 13: Further, the chlorophyll−a and Nodularia biomass increase in the late summer is preceded by a peak in Fe(II) concentration and a small peak in NH4 (Figs. 6a, b, 9a), which together with a shallower thermocline and N inputs from rain and senescent cyanobacteria, may have induced a second growth period for phytoplankton.

Because the data are spread over multiple graphs it is confusing. Furthermore, do the authors mean that the observation of a second growth period of phytoplankton is based on an increase in Chl a and Nodularia biomass and that a peak in Fe(II), NH4 and N inputs from rain and senescent cyanobacteria may be responsible for this? How could it be concluded that Fe(II), with reduction and oxidation kinetics on a time-scale of minutes, and varying with other factors as light, pH, oxygen and H2O2 on a time scale

of a day be shown to be responsible for a phytoplankton bloom sampled on a time scale of weeks? The authors may be right but the data don't show it. Furthermore, are there any other factors that are not mentioned here that may induce an increase in Chla and biomass like e.g. an increase in irradiance due to better weather, or higher temperatures, especially as the concentration NH4 and nitrate seem to stay at a pretty constant level during the study period (Figure 9a)?

43) p3826, line 8-13: here the relative importance of locally produced siderophores increases with the decrease of total ligand concentrations. We suggest that local production of iron chelators may hence counteract the overall loss of humic substances by processes such as photoreduction and export over the summer that mainly enter the Baltic Sea via high fresh water input during spring time (HagstrÂÍom et al., 2001; BergstrÂÍom et al., 2001).

The authors state that the local biological production of Fe chelators counteract the loss of humic substances. . ...however the authors don't evaluate, based on literature or their own data, what the magnitude of loss of humics could be in the Baltic Sea? Furthermore to counteract this loss the local production of Fe chelators, siderophores as the authors specify them, should be of a similar magnitude as the loss in humics. However, as far as I know there is very little quantitative information on the rate of locally produced Fe-chelators/siderophores. It has been reported that the Fe-binding capacity increased rapidly after iron fertilization, however, this could also be the result of the binding of Fe to Fe colloids as suggested by (Boyé et al., 2005). The only information available is that in the open Atlantic Ocean the detected Fe-siderophore concentration only contributes between 0.2-4.6% of the dissolved Fe fraction (Mawji et al., 2008). This aspect needs more discussion in relation to existing literature.

4.3.2 Loss of Fe(III) organic ligands and H2O2 production

44) p3827, line 13: Ligand-metal charge transfer and successive release of Fe(II) from the organic complex during photoreduction can further result in ligand destruction by

irradiance, which results in H2O2 production (Abele-Oeschger et al., 1997).

I could not find this specific information in the given reference?

45) p3827, line 15: Our data show that H2O2 values coincide with Fe(II) in the upper part of the water column and indicate such mechanism (Figs. 3f, 4f, 5e).

Coinciding concentrations of H2O2 with Fe(II) could just be the result of independent reactions based on irradiance? What about alternative sources of Fe(II) like colloids?

46) p3828, line 9: Further, Fe(II) is readily consumed by heterocystous cyanobacteria, as indicated by the low Fe(II) concentrations in the incubations that were enriched in cyanobacteria and the progressive increase in Fe(II) in the treatments that were depleted of this group (Fig. 11b).

Again the authors do not discuss alternative explanations for their observations. Yes, maybe the Fe(II) is consumed by the cyanobacteria. Alternatively, addition of the cyanobacteria to the experimental seawater may have induced adsorption of the Fe(III) to the cell wall of the cyanobacteria resulting in the unavailability of the Fe(III) for photoreduction. More discussion is needed.

47) p3828, line 15: as was observed for diatom species in the Southern Ocean (Rijkenberg et al., 2008).

The authors of this reference did not observe increased Fe(II) by diatoms in the Southern Ocean. They observed increased Fe(II) concentrations in incubations that they performed using Southern Ocean seawater.

Paragraph 4.3.3 Factors controlling Fe(II) concentrations

48) p3829, line 3: Therefore, we imply that Fe(II) deposited or produced during this period may have been maintained at elevated levels by hampered Fe(II) oxidation rates due to organic Fe(II) complexation.

As the authors don't give any information on their calculations, the assumptions that

they made, the timing of rain events as compared to Fe(II) sampling, discussion of any alternative explanations etc it is very difficult to accept their conclusion.

5 Conclusions

49) Discussion of the nutrient ratios etc should be transferred from the conclusions to the discussion section.

50) Concerning the following conclusions:

i) However, the relatively high iron concentrations compared to macronutrients may not be directly accessible to phytoplankton. Thus, Fe(II) appears a major role in iron acquisition by phytoplankton, namely diazotrophic cyanobacteria, in the Baltic Sea. ii) The photochemistry of this micronutrient further also counteracts losses by colloid and particle formation of bioavailable iron in the LMW fraction during bloom development, given that such a mechanism as identified for other trace metals also affects iron biogeochemistry in the Baltic Sea (Ingri et al., 2004). iii) a large fraction of the bioavailable iron is supplied by Fe(II). iv) Fe(II) is supplied by rainwater v) Fe(II) is maintained by Fe(II)-complexation

For conclusion ii) are no data and it is not discussed in the manuscript.

At this moment, as presented by the authors in this manuscript, I am not convinced that their data can support their conclusions (i-v).

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