**Biogeosciences
Discussions**

# *Interactive comment on* "Labile Fe(II) concentrations in the Atlantic sector of the Southern Ocean along a transect from the subtropical domain to the Weddell Sea Gyre" *by* G. Sarthou et al.

**G. Sarthou et al.**

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We thank the three anonymous reviewers for their insightful comments, which greatly helped to improve the manuscript. All comments have been addressed below and, when needed, in the text.

Anonymous Referee #1

1) Page 4177, line 1-11. The authors discussed some possibilities that atmospheric input might affect the labile Fe(II) distributions. In the previous manuscript (Chever et

C2308

al., 2010), the atmospheric dust transport model was successfully applied to discuss DFe sources, but I don't think this approach is suitable for considering the surface Fe(II) distributions because Fe(II) half life time is too short (2.9 – 11.3 min). If any information of wet deposition in these regions during this cruise, it might be useful for the discussion on surface labile Fe(II) distributions.

We agree that the dust transport model used for DFe in the Chever et al article can not be applied here and that information on wet deposition would be very useful for the discussion on our surface labile Fe(II) concentrations. Unfortunately, we do not have this kind of information.

2) Page 4178, line 8. In Figure 7, biogenic particulate barium data are shown, but the relationship between Baxs and Fe(II) profiles has not been explained clearly.

Baxs can be used as a proxy for remineralisation, similar to the 234Th/238U ratio. Indeed, it is believed that microcrystalline barite represents a sensitive tracer of organic matter breakdown in the mesopelagic zone, since the breakdown of the aggregates releases barite crystals and maintains a Baxs maximum occurring generally in the 100–600 m depth region (Dehairs et al., 1992). A sentence has been added to clarify the relationship between Baxs and labile Fe(II).

3) Page 4178, line 15-23. To discuss the remineralization process of biogenic particles, the authors examined the relationship between Fe(II) and AOU in sub-surface maxima. However, AOU is not a good indicator for the remineralization process near the surface layer. If nitrite and ammonium in seawater were determined at the same stations, it might be useful to compare the profiles of labile Fe(II) with those of nitrite and ammonia because nitrite and ammonia are also released during the remineralization process of biogenic particles.

Both reviewers (#1 and #3) suggest that AOU is not a good tracer for the remineralisation near the surface and that the non-correlation between Fe(II) and AOU is not unexpected. We thus decided to remove this paragraph.

C2309

Ammonium concentrations were measured during the cruise. All profiles showed sub-surface maxima located between 35 and 120 m, which did not coincide with neither the labile Fe(II) nor the 234Th/238U maxima. This could be due to the time-scale difference between the different processes.

4) Page 4179, line 3-5. As the authors mentioned, concentrations of some elements in AAWW and AASSW might be different because of biological uptake. However, it would be difficult to connect Fe(II) concentrations with the seasonal variation of water masses since the half-life time of Fe(II) is too short. Some explanation is needed to understand the time-scale differences.

We agree that the formation of WW is at a seasonal time scale and we modify this paragraph to take into account the time-scale difference: "In the southern part of our transect (stations L6, S4, L7, S5, Fig. 8), the winter waters were strongly visible on the T data and were associated with local minima of labile Fe(II) concentrations. Although the formation of the winter waters is on a seasonal time-scale and labile Fe(II) is a transient element, biological activity is lower in the winter water and the lower concentrations of labile Fe(II) in these water masses may reflect processes involving a biological source of Fe(II) in the AASSW and confirm results observed in the SML."

Technical corrections. 1) Page 4167, line 11. "Hansard et al., 2009)" should be "Hansard et al. (2009)". 2) Figure 4. The range of the y-axis is too wide. It is very difficult to see the difference of the slopes.

Done.

Anonymous Referee #2

P. 4169, Line 10. Section 2.2 Sample processing and analytical methods. In this section the authors discuss the time between sub-sampling and analysis was 3 min. How exactly did this happen. Was each Go-Flo sampled individually prior to the next Go-Flo being recovered from the Kevlar line? Also, how long would it take to recover the

Go-Flo bottles before they were sampled, this is mentioned later on in the manuscript but it would also be useful to mention it here for clarification of the actual time between collection and analyses.

Each Go-Flo was not sampled individually prior to the next Go-Flo being recovered from the Kevlar line, but rather, when all the Go-Flo bottles were in the clean container, sub-samples were taken from each bottle and immediately analysed. Since the time between the tripping of the Go-Flo bottles and analyses (30-40 min, see the response to reviewer # 3) stood for the surface samples, we preferred to put this sentence in the discussion concerning the surface mixed layer (section 4.2.1.).

P. 4169, Line 27. With regards to the method used for the determination of Fe(II), I believe this was originally used by King et al. (1995) and adapted by Croot and Laan, I therefore think this should be included as a reference along with Croot and Laan (2002).

The reference King et al. (1995) has been added in the text.

P. 4173, Line 16 and Figure 5. I think the depth of the intermediate depth shown in Fig 5c needs to be confirmed, in the legend it states 300-2000m but the manuscript text and figure caption, the depth is stated as 500-2000m. In addition, I don't think the authors have made reference in the text to the oxidation rates calculated for below 2000m as shown in Fig 5c.

Indeed, it was a mistake. In the text and the figure caption, 500-2000 m was replaced by 300-5000 m. The reference to the oxidation rates below 2000 m was made in the text by the sentence: "At the four super stations where two different depths were sampled below 300 m, values were not significantly different (paired t-test, P=0.6, n=4)."

P. 4176, Lines 14-30. The authors present very good reasons for the high Fe(II) values observed at the stations sampled between 12:00 and 16:00. They discuss biological production and indicate some superoxide and Fe(II) production rates which I think are

realistic. Whilst I understand the half life for superoxide is also low, as the samples analysed were unfiltered, could there have been some positive interference from superoxide generation which could also account for the high Fe(II) values observed.

As stated in the section 2.2, the presence of superoxide can indeed induce an overestimation of labile Fe(II). The sentence (p. 4176, line 23) has been changed to take this effect into account: "The potential production rates of superoxide were thus likely sufficient to drive Fe(II) production." has been replaced by "Although inducing a potential overestimation of the labile Fe(II) measurement, the production rates of superoxide were thus likely sufficient to drive Fe(II) production."

P. 4177, Line 1. I think it might be useful to include the dates of the ANT XXIV/3 cruise to clarify that the time periods referred to coincide (Feb-Apr 2008).

The dates have been added: 10 Feb.-14 April 2008

P. 4177, Line 17. Could the authors please clarify what the labile Fe(II) ranged quoted (0.023-0.87 nM) refers to, is this the sub-surface maxima observed in the STZ or in the ACC, if it is the STZ what was the range for the ACC.

The range referred to the ACC. For clarification, the sentence has been changed and is now: "Although generally lower than in the STZ (0.076-0.125 nM), sub-surface maxima were also observed in the ACC (0.023-0.087 nM) and north of the Weddell Gyre (0.025 nM) at depth between 60 and 300 m."

Figure 3. The x-axis on Fig 3a is labelled DFe (nM), should this not be titled 'labile Fe(II)'.

It has been changed.

Figure 6. Title of the y-axis, this refers to a % so I do not think the '(nM)' is necessary.

It has been changed

Anonymous Referee #3

In this context, it is not clear to me what information the loss of the added Fe(II) provides. Is the loss rate thought to be representative of the rate of oxidation of Fe(II) at ambient concentrations? Or, does it tell us how quickly a water sample needs to analyzed after subsampling/initial collection? In either case, I'm not convinced that such operationally defined half-lives are very useful, and I would urge the authors to give this issue more thought, and to then clearly articulate what the calculated half-lives actually represent. The comparison with model-derived Fe(II) oxidation kinetics implies that they provide estimates of ambient Fe(II) oxidation rates, although one might argue that perturbing the solution by adding relatively large spikes of dissolved Fe(II) standard could confound such estimates.

The half-life time as defined in our study gives information about the rate of oxidation of Fe(II) at (sub-)nanomolar concentrations. Comparison of this value with theoretical values allow us to estimate a potential effect of organic complexation on the oxidation rates. To clarify this point, a sentence has been added: "The half-lives ($t_{1/2}$) were then calculated as $t = \ln(2)/k_{ox}$, for the four Fe(II) spikes (Fig. 5, Table 3). They will give information on the oxidation rates of Fe(II) at (sub-)nanomolar concentrations and will then be compared to theoretical values."

1. The reported limit of detection (<0.01 nM) is remarkably low for a flow injection method without using preconcentration. Given that, I'd like to see a few more details provided, as well as on the precision of the analytical method. Was the aged seawater sample filtered? Was this detection limit calculated from repeat analyses of aged seawater conducted during a single day only (my reading of the text)? Were there day-to-day variations in sensitivity and reproducibility?

The detection limit was calculated as three times the standard deviation of the blank measured using a 24 h aged unfiltered seawater sample. The blank was not calculated from repeated analyses of aged seawater conducted during a single day but was determined each day. Blank values ranged from 14 to 72 pM with a mean value of $36\pm12$ pM. The detection limit ranged from 1 to 28 pM with a mean value of $9\pm6$ pM

(n=29). This information was added in the manuscript. For an aged seawater sample, the reproducibility was typically better than 5% and did not vary from day to day. On the contrary, the sensitivity has varied during the whole cruise by a factor of 6, which is typical for a Fe FIA measurement. Below is an example of the peak height of the 1 nM Fe standard during the cruise. We do not think that this information is necessary in the manuscript and did not add it.

2. Were any comparisons made between unfiltered and filtered samples? This seems an obvious experiment to investigate whether particles in unfiltered samples were responsible for production or loss of Fe(II).

At the two first stations (L1 and S1), both dissolved and labile Fe(II) concentrations were measured and dissolved Fe(II) was systematically lower than labile Fe(II) and close to the detection limit. We could not know if this was due to rapid oxidation after filtration or to the particle effect. As we could not manage to do both types of measurements because of time restriction, we chose to only measure labile Fe(II).

3. In the introduction, it is stated that Fe has been 'shown' to limit primary production over >50% of the world ocean (with Boyd and Elwood, 2010, cited). Maybe 'suggested' is a more accurate way to say this?

It has been changed on the text.

4. The text contains some minor grammatical errors that should have been corrected prior to submission, given that at least one of the authors is a native English speaker.

The text has been carefully read by the native English speaker co-author and the minor grammatical errors have been corrected.

5. A larger locator map (for context) would be useful in Fig. 1, as would names on the landmasses shown.

Figure 1 has been changed.

6. The H2O2 manuscript in preparation should be cited as 'in prep' if it has not yet been submitted.

It has been changed in the text and the reference list.

7. Fig. 3a is labeled 'DFe', whereas the text and caption indicate that the figure shows labile Fe(II).

Figure 3 has been changed

8. There seems to be some mismatch between the color key shown in the ODV plots of Fig. 3 and the values that are cited in the text; for example: Text cites Fe(II)/DFe values of 40-67% in SML at S3, S4, S5, whereas colors in Fig. 3b don't match these values. The Fe(II) concentration of 0.125 nM at S2 at 196 m does not correspond to the color shown in Fig. 3a. Similarly, the 30-70% Fe(II)/DFe values cited in text do not correspond to colors shown in Fig. 3b.

The data set for the ODV plot is the same as in Table 2. The apparent discrepancy results from the ODV interpolation algorithm, which smoothes the data.

9. Having Fe(II) presented in both nM and pM units in Table 4 is confusing; better to use just one concentration unit (either nM or pM) throughout the text.

Table 4 has been changed and nM is used in the Table and throughout the text.

10. Did it really take only 15-20 minutes between the sampler closing and the sample being analyzed? This seems like an underestimate, given that the samplers were deployed on a line.

The three stations we were interested in were stations S3, S4, and S5. The surface casts were done at a maximum depth of 840, 550, and 860 m, respectively. The 15-20 min range time was estimated using microcast data. It was the time between the sending of the first messenger and the recovering of the first two bottles. However, the reviewer is right because this is not the time between the tripping of the Go-Flo bottles

and the analyses. Indeed, the sampling of the Go-Flo bottle only started when all the bottles were in the clean container. Having a new look on the microcast data gives a time of 30-40 min. This does not change the argument that the theoretical labile Fe(II) data is even larger, but the time intervals have been changed in the text.

11. The comparison with 234Th/238U profiles as evidence of Fe(II) production via remineralization is nice.

It is indeed the first time that such a correlation is evidenced.

12. The non-correlation between Fe(II) and AOU is not unexpected, given that AOU is an integrative measure, versus the transient nature of Fe(II).

We agree and this has been removed from the manuscript (see answer to reviewer # 1).

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Interactive comment on Biogeosciences Discuss., 8, 4163, 2011.

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