

Interactive comment on “Solubility of iron and other trace elements over the Southern Indian Ocean” by A. Heimbürger et al.

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We would like to thank reviewers for their constructive comments, which allow us to improve our paper. We present here responses to these comments.

Reviewer #1

1) “General remarks: This article contains relevant and recent scientific questions and should be published by Biogeosciences after revision. However several abstracts need to be re-written to clarify authors really mean in them. I also think that the title needs to be altered as at present it is formulated very loose. My biggest concern with this manuscript though is that I do not really know what the authors mean with the term solubility as it is used in a different meaning between e.g. the atmospheric and

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oceanographic communities (see also the publication by Baker and Croot, is cited in the present manuscript). The manuscript at present states this term with a simple percentage and it should at least once be explained what exactly is meant with it ”

Solubility is defined by the equation (1) in paragraph 3.1. Such definition is recently used for rainwater samples in Buck et al. 2010b (paragraph 3.7) and before e.g. in Lim et al. 1994 in paragraph entitled "Definition of Trace Metal Solubility in Precipitation" p 354. Our definition of solubility is related to the "fractional solubility" defined by Baker and Croot 2010 for laboratory experiments on dissolution of aerosols. We added three sentences in section 3.1. (page 6073), just after the formula of the solubility, to define what we consider as the soluble fraction of rain and the insoluble one and in order to explain more clearly what is our definition of solubility: “The soluble fraction is defined here as the amount of metals in rainwater which passes through the 0,2 μm PC membrane filter. The insoluble one is defined as the amount which stay on the PC filter. If we assume that rainwater is aerosol particles trapped in water drops, solubility is then defined as the fraction of metals that is dissolved in rainwater (i. e. the metal content in the filtrated rain divided by the total metal content in rain) (e.g. Lim et al., 1994; Buck et al., 2010b). This solubility is related to the "fractional solubility" defined by Baker and Croot 2010 for laboratory experiments on aerosol dissolution. Filtration of rainwater during the sampling provides a direct measurement of natural solubility.”

2) “It also would be very useful to know why the different trace elements measured were chosen and what their biogeochemical relevance is.”

See responses to special comments (P6066 L8 and P6076 L22).

3) “Furthermore the results obtained in the study should be discussed in more detail and also linked to the presented figures.”

We think that this comment is for the Figure 4 only. So, we applied this advice for the Figure 4 (page 6075). This paragraph is also changed in order to response to Reviewer#2 comments: “Rain samples may be contaminated by local soil emission

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due to human activities on PAF occurring not far enough from the sampling site: soil portions are occasionally moved for track maintenance generating exposed surfaces that produce local emission spots. Heimbürger et al. (2012a) demonstrated that Ti/Al ratio is a suitable tracer for such contamination: the authors reported that these ratios are equal to 0.15 ± 0.05 (mean \pm s) and 0.04 ± 0.01 in soil and atmospheric deposition samples respectively. Consequently, the $[\text{Ti}]_{\text{total}}/[\text{Al}]_{\text{total}}$ ratio was computed for each rain sample (Fig. 4). Uncertainty on this ratio was computed by the following formula: $\sigma(\text{Ti}/\text{Al}) = (\text{Ti}/\text{Al}) \sqrt{((\sigma \text{ Ti total})/\text{Ti})^2 + ((\sigma \text{ Al total})/\text{Al})^2}$ (8) with $\sigma(X \text{ total}) = \sqrt{(\sigma X \text{ soluble})^2 + (\sigma X \text{ insoluble})^2}$ (9) Rains from P6_09 to P5_08 on Fig. 4 present Ti/Al ratios consistent with the one found in Kerguelen's soil, which is not compatible with pure long range transported particles, and so they were not discussed afterwards. Rain P3_10 exhibits a Ti/Al ratio incompatible with local soil contamination and in the range found in deposition samples (Heimbürger et al., 2012a). Four rains (P1_10, P3_08, P6_08, P3_09) have a Ti/Al ratio between the ones in soils and deposition. If we take into account standard deviation calculated with the Eq. 8 and Eq. 9, a local soil contamination is less probable for P1_10 and P3_08 than for P6_08 and P3_09, for which a small recovery of ranges of both soil and samples is observed. Because no other strong discriminating criteria was found for these four rains, they will be included with rain P3_10 in the following discussion."

We changed caption on Figure 4: "Ti/Al in P3_10, P1_10, P3_08, P6_08 and P3_09 exhibit values not compatible with the range of Ti/Al found in soil collected on Kerguelen Islands; these five rains were then considered as not significantly influenced by local soil contamination and so representative of long range transport."

We also changed the next paragraph (page 10 lines 277-281) and added a table (Table 2), which presents sampling conditions of the five selected rains: "To insure that no other local contamination from anthropogenic activities taking place on PAF, we used gdas re-analyzed archives (Draxler and Rolph, 2012; Rolph, 2012) to observe wind

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direction during the respective sampling times of the five kept rains. The base PAF is located East of the sampling site. For these five rains, winds came from opposite sectors of PAF, excluding wind transported contamination from the base (Table 2)."

4) "Why for example shows Figure 4 such big error bars?"

We done a tipping mistake on formula to compute error bars. We corrected it and so we found smaller error bars, which depend on the both soluble and insoluble concentrations in samples, detection limit of an elements, measurement reproductivity and accuracy. To found $[\text{Ti}]_{\text{total}}/[\text{Al}]_{\text{total}}$ standard deviation, we compute $\sigma([\text{X}]_{\text{total}})$ and then $\sigma([\text{Ti}]_{\text{total}}/[\text{Al}]_{\text{total}})$ with the formulas givent above. We added these both formulas on our articles to explain how to obtain error bars on Figure 4 as you can see on the answer we done for the reviewer's comment just above.

5) "Specific comments: I recommend including the word "rain and/or aerosol" in the title as the formulation "over the Southern Indian Ocean" is confusing." We changed the title of our article as suggested by the reviewer: "Solubility of iron and other trace elements in rainwater collected on Kerguelen Islands (South Indian Ocean)".

6) "P6066 L8: Somewhere in the manuscript should be stated why this combination of trace elements was chosen ."

In order to add this information on the manuscript, we added several sentences in different parts of the text to explain this choice: page 6072: "Table 1 presents DL, RSD% and RR% for a set of analysed elements, for which results were validated (see section 3.1) and so discussed afterwards"; page 6073: "It has to be noted here that others elements (Co, Cr, Cu, Ni, V, Pb, Zn) were also analysed in rainwater but their ratio values (median quantity in blanks relative to the one in rainwater) were higher than 40 % for the both soluble and insoluble fractions, and even equal to 100 % for Ni and Cu. Thanks to all the blanks we performed, this contamination was identified as coming from PC filters. Although careful washing of these filters, filter blank exhibit high quantities of Co, Cu, Cr, Ni, V, Pb and Zn compared to the median quantities found in rain samples

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for these elements after blank corrections. It leads to a contamination of the soluble fraction of laboratory and field blanks, for which no other significant contamination were observed.”; paragraph 3.4 (beginning): “Before this study, no observed solubility values in rainwater were available in the literature for the oceanic area of Kerguelen Islands. Our values can help to better quantify and model (chemistry and transport) the part of atmospheric iron, which can be bioavailable for phytoplankton in the Southern Indian Ocean.”; paragraph 3.4 (end of the first paragraph): “High solubility of Ti informs us that dissolution processes in the atmosphere are very efficient and probably destroy all the solid phases forming original aerosols, including the ones containing REE.”

7) L10: 70% of what? The weight of the aerosols?”

The 70% is a solubility value (fraction of the dissolved part of aerosols in rainwater). We changed the sentence: " The solubilities of elements" instead of " The solubilities".

8) “P6067 L1-3: This sentence needs more explanation as it is hard to understand what the authors mean with it”

We changed this sentence by: “It is often assumed that the dissolved forms of trace metals in atmospheric deposition are directly available for phytoplankton because bioavailability is difficult to measure (e. g. Shi et al. [2012]). Indeed, bioavailability depends on several factors, which have to be taken into account to determine it, such as the presence of others nutrients in euphotic surface waters, the residence time of deposited atmospheric particles in surface waters, the soluble fraction and the physicochemical speciation of trace metals in seawater (Boyd, 2002; Boyd et al., 2010). Even if phytoplankton only uses a fraction of atmospheric soluble trace metals in its metabolism (Visser et al., 2003), the best proxy so far is taking the soluble fraction of metals as the bioavailable part of these metals for marine biota (Shi et al., 2012). This dissolved fraction expressed as percentage is referred to as “solubility”, for which definition depends on the considered science field (e. g. oceanographic and atmospheric sciences) and the usage context. In this paper, we will define solubility in section 3.1.”

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9) “P6068 L1: insert “and” before direct measured”

The sentence here is: “the authors found that direct measured dust flux is 20 times higher than the previous estimation calculated by Wagener et al. (2008)”. We think that no “and” before “direct measured” have to be added.

10) “L8+9: Rewrite this sentence like: To our knowledge up to now such measurements have never been taken over this oceanic region”

We replaced the sentence by the one proposed by the reviewer.

11) “P6069: Delete washing in the title”

It is done.

12) “L7: supplier of the filters?”

Filters are standard polycarbonate filters inserted in a special device of two polycarbonate rings. This is explained at the end of the last paragraph of the section "clipped with special rings (FilClip®).

13) “P6071 L5; why was the pH only 2008 measured and not in the later campaigns as well; this supplies essential information”

pH have to be measured on the field immediately after sampling. No accurate nor repeatable pH measurements were possible during the other campaigns. Our instruments malfunctioned probably because of hard transportation conditions (high temperatures encountered in ship containers), which damaged our electrodes. We only succeed pH measurements during the 2008 campaign.

14) “P6072 L6: replace “The” with “These” and “too” with “as well””

Done.

15) “ L22: replace “turned out to be” with “were””

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Done.

16) "L25: reference for the geostandards; where can this information be looked up?"

You can find certified values for these geostandards directly on the website of the SARM laboratory and USGS. Certificates are published on the web sites of the institutions: <http://helium.cirp.cnr.fr/SARM/pages/geostandards.html#> for SARM (all geostandards) http://crustal.usgs.gov/geochemical_reference_standards/mica.html (USGS, SDC-1)

Because web page addresses are volatile, we did not refer it but added some information to a better chance to find the certificate for the reader (page 6, lines 180-181): "BE-N (Basalt from SARM laboratory, France) and 8.6 mg of SDC-1 (Mica Schist from USGS, USA) geostandards"

17) "P6075 L5: short explanation how this can happen"

We added some information: "Rain samples may be contaminated by local soil emission due to human activities on PAF occurring not far enough from the sampling site: soil portions are occasionally moved because of track maintenance generating exposed surfaces that produce local emission spots."

18) "L18: Add: Only the 3 not contaminated samples will be further discussed"

We deleted this sentence because we changed this paragraph in order to give responses to comments of Reveiwer#2.

19) "P6076 L6: add for the three not contaminated"

We changed this sentence because we have improved the rejection criterion of contaminated rain samples which was criticized by Reviewer#2.

20) "L22: add here for example why each of this metals were measured and what specific information each can contribute"

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We already added information about the choice as explained above in previous answer of Reviewer#1 comment (P6066 L8). Iron is directly involved in biota and other elements are useful to understand and model the chemistry of dissolution processes. We added information where the reviewer asked: "Before this study, no observed solubility values in rainwater were available for the oceanic area of Kerguelen Islands; our values can help to better quantify and model (chemistry and transport) the part of atmospheric iron, which can be bioavailable for phytoplankton in the Southern Indian Ocean" and "High solubility of Ti informs us that dissolution processes in the atmosphere are very efficient and probably destroyed all t the solid phases forming original aerosols, including the ones containing REE."

21) "L26-28:Reword or split this sentence"

We slightly rewrote this sentence: "It is believed that during their transport in the atmosphere aerosols typically undergo around 10 condensation/evaporation cloud cycles (Pruppacher and Jaenicke, 1995). In clouds, trace gases, such as HNO₃, SO₂ and NH₃, are present and modify the pH of cloud droplets, which can increase the soluble fraction of mineral particles."

22) P6077 L10: Please insert a reference for this statement

We added the reference Baker and Jickells 2006.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/10/C2907/2013/bgd-10-C2907-2013-supplement.pdf>

Interactive comment on Biogeosciences Discuss., 10, 6065, 2013.

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