Biogeosciences

Discussions

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Interactive comment on "Solubility of iron and other trace elements over the Southern Indian Ocean" *by* A. Heimburger et al.

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

Reviewer #2

1) "General comments. 1) Data presentation and discussion in this manuscript are not enough to support reader's understanding. Authors lead discussion to conclude that high soluble fraction of TM concentrations in rain water is due to fine dust particle, which is more transportable to remote area and more soluble than the larger dust fraction. To lead this conclusion, authors determine that three rain samples were free from local contamination by using definition of Ti/Al concentration ratio. Then, they

only discuss for these three rain data. However, two of the Ti/Al ratio (rain P1_10 and P3_08) are slightly over the range of the dust deposition. Only using these three values for discussion is not persuasive for reader to reach the conclusion."

We did not demonstrate that fine particles are responsible of high encountered solubilities. We only cite this hypothesis observed by Baker and Jickells (2006) and Ito (2012) which is consistent with our solubility observations. We slightly changed this sentence: "Indeed, Wagener et al. (2008) and Heimburger et al. (2012a) noted that particles observed on Kerguelen Islands at sea or ground level exhibit 2 μm median diameters, suggesting that only the fine dust fraction, which is believed to be more soluble than the larger dust fraction, reaches Kerguelen Islands."

Very remote atmospheric sampling is a real challenge. Concentrations of trace metals of interest are very low and very easily modified by contamination. Our goal in this paper is to determine the solubility of TM emitted by continental sources and transported over thousands of kilometer away. Because we used manually devices, we cannot sample rainwaters far from an human installation including possible local contamination sources. As we stated in a previous paper (Heimburger et al. 2013), automatic samplers have to be deployed to completely avoid anthropogenic perturbations. In this case, such samplers do not exist at the required level of cleanliness and with on line filtration. We worked around this problem using a screening method discarding "bad" samples. Ti/Al ratio was found to be the best parameter to discriminate clean and locally contaminated rainwater samples. Our first criterion introduced some doubt on the validity of the test. We changed the criterion in "measured Ti/Al ratio in sample have to be less than the lower range limit of Ti/Al ratio in soils", and in consequence two more rainwater samples were added in the discussed data set. We modified the text of paragraph 3.2 to be clearer in our explanation of the criterion: "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 lo-

cal soil contamination and in the range found in deposition samples (Heimburger 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. Âă8 and Eq. Âă9, 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. Nevertheless, no strongly discriminating criteria was found for these four rains, they will be included with rain P3_10 in the following discussion (insoluble and soluble concentrations of these five selected rains are available in supplementary reading)."

2) "In discussion, authors describe some for wind roses and air mass back trajectories simulation, but they did not show these data for presentation in this manuscript. I think, authors should present all 14 rain TM data (not only calculated flux but also concentrations of TM, volume of collected rain water, period of each rain event) with other environmental information such as wind roses and air mass back trajectories. Then, they should lead discussion step by step to reach their conclusion. Additionally, authors can compare the proportion of soluble fraction in their rain water sample to reported other oceanic and coastal data (in the Atlantic, and the Pacific), and extract a characteristics of remote Southern Ocean dust wet deposition (see specific comment #11)."

Discarded samples are really discarded because they are contaminated by local soils with a high probability. With the modified criterion, we separated rainwater samples in two groups and explained that rainwater samples possibly contaminated by local soil emission exhibit a much lower solubility than the one found in not or not significantly contaminated samples (page 6076). Addition of the two rains P6_08 and P3_03 does not change conclusions: "Solubilities in rains are reported in Table 4: they are higher than 70% for all the elements (Al, Ce, Fe, La, Mn, Nd, Ti) for the five considered rain, except for Ti (33% $\pm$ 44% and 46% $\pm$ 32%) and Fe (57% $\pm$ 17% and 51% $\pm$ 22%) in P1_10 and P3_09 respectively. The rare earth elements (La, Ce and Nd) also exhibit

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high solubility values ranging from 68% to 98%. In contrast, solubilities measured for the rejected rain samples show much lower values, for example with a median of 17% for Ti, 9% for Fe and 30% for Al."

We agree to publish more information on our "good" samples (not or not significantly contaminated samples by local soil emission). We added a new table (Table 2), which presents sampling condition of the five kept rains, and a table in supplementary reading giving measured rainwater concentrations found in these rains. We also join to this answer all the data the Reviewer#2 asked but for his private usage only; the following table present quantities (ng) found in blanks and in samples (blank subtracted).

For the comparison with data in literature, see answer of the special comment 11. For wind roses and trajectories, see answer of the specific comment 12.

3) "2) Authors use the word of "solubility" through the manuscript. They should take care of this word more carefully. Many studies over the years have examined via dialysis or filtration experiments to determine the "solubility" which is the proportion of soluble iron that was leached from particulate fraction (e.g. Byrne and Byrne and Kester, 1976; Crecelius, 1980; Chuang et al., 2005; Buck et al., 2006; Wu et al., 2007), or maximum capacity of iron which can be soluble in seawater (e.g. Kuma et al., 1996). However, data reported in this study is measurement of TM concentration in soluble fraction (TM in 0.2 um filtrate) and particle fraction (TM on the 0.2 um filter) in the rain water, and only calculated a ratio of Sx%. This is just a proportion of the soluble fraction in the total fraction (%). This is not same as "solubility" which obtained by dialysis or filtration experiments, and Sx% in this study can't compare directly to the reported "solubility". Authors did not measure the "solubility" in the rain water as same definition by experimental method. Therefore, they should use the word "solubility" more carefully. They should compare their data to previous reported "solubility" more correctly."

This comment is similar to the first of Revewer#1, see also response to Revicer#1. Solubility is defined by the equation (1) on paragraph 3.1. Such definition is recently used

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for rainwater in Buck et al. 2010b (paragraph) 3.7 and before e.g. in Lim et al. 1994 in the paragraph entitled "Definition of Trace Metal Solubility in Precipitation" p 354. Our solubility is related to the "fractional solubility" defined by Baker and Croot 2010 for laboratory experiments on aerosol dissolution. We added three sentences in section 3.1., just after the formula of the solubility, to define what we consider as the soluble fraction of rain and the insoluble one and what is our definition of solubility (paragraph 3.1): "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 from aerosols in rainwater (i. e. the metal content in the filtrate divided by the total metal content of aerosols in rain) (e.g. Lim et al., 1994; Buck et al., 2010b). This solubility is related to "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." (as answered to Reviewer#1 comment).

Like many other authors, we used filtration to separate soluble and insoluble parts in wet deposited material. An added value of our work is that we performed rainwater filtration directly during the rain event which limit further chemical evolution of a bulk multiphasic rainwater. We compared our values with both solubilities of aerosols and of aerosols in rainwater, so directly comparable with our values. The only differences between these study and our work is the way to collect aerosols (on filters by air filtration, rain collection) and the method i) to extract the soluble fraction for aerosols filtration and ii) filter rain (directly as done here, just after the sampling).

4) "3) I think, the most valuable point of evaluation of wet TM deposition flux is comparison with total dust deposition flux (which include dry deposition), and estimate contributions of the wet deposition, quantitatively. In this aspect, authors has enough data set for total dry deposition from same field campaigns (Heimburgur et al., 2012)."

Our sample is pure wet only deposition because we sampled rainwater on an event

basis. Dry deposition in the area was estimated in a previous work with a time series (Heimburger et al. 2012a) and found to be negligible. Comparisons with total deposition measured in this previous time series was made only to check if collected rain samples are in agreement with an average deposition flux (see next answer).

5) "In this manuscript, they try to compare mean calculated value of Al and Fe in both wet and total fluxes in discussion (section 3.3). However, comparison of average values of all data set are not suitable for this evaluation. Because unit of the total deposition (μg m-2 day-1) is different from the unit for wet deposition (μg m-2/(event basis)), these two values can not be compared directly. I think, comparison between total and wet deposition during each campaigns period (each campaign bases) are more suitable to show the contribution of wet deposition to total deposition flux. Then, authors can compare the wet/total deposition flux among each field campaign."

We replaced Al and Fe deposition values found by Heimburger et al. (2012a) by the ones documented in Heimburger et al. (2013, now published) and averaged over three different sampling sites, which exhibited same flux values for these both elements. Indeed, in this second paper, we done a complete work on uncertainties associated to flux values, which allow us in this paper to better compare our rain flux values with our previous values. We divided values from Heimburger et al. (2013) by the frequency of rain events found on Kergeuelen Islands in order to obtain fluxes in μg/m^2/rain event. Because we consider five rain samples yet in our manuscript (and not three as proposed in the first version of this paper), mean flux values in rainwater slightly changed.

We were not clear enough in the text concerning comparison between averaged flux and per event flux. We changed the text as follow (3.3): "Deposition fluxes generated by single rain events were computed by dividing the quantities found in each validated rain sample by the surface of the funnel aperture (0.045 m^2). In Heimburger et al. (2013), the authors found that atmospheric total deposition fluxes, averaged over 2009-2010, are equal to 53 $\pm$ 2 μg m-2 d-1 and 33 $\pm$ 1 μg m-2 d-1 for Al and Fe respectively and for the oceanic area of Kerguelen and Crozet Islands. Here, we found averaged rain fluxes

(wet fluxes) equal to (mean Â ă±Â ă σ) 24 ± 18Â ăμg m-2 per rain events for Al and 14 ± 10Â ăμg m-2 per rain events for Fe (TableÂ ă3). Because dust deposition is controlled by wet deposition on Kerguelen Islands (Heimburger et al., 2012a), we can neglect dry deposition flux and we can assimilate total deposition fluxes to the wet deposition ones. Taking into account meteorological data that we recorded 8Â ăkm from PAF, rain events occurred from once a day to every two days, and so with a frequency of 0.5 to 1 per day. Applying this frequency on deposition flux values from Heimburger et al. (2013), the averaged deposition flux on Kerguelen Islands is from 51 to 110 μg m-2 per rain event for Al and from 32 to 68 μg m-2 per rain event for Fe, which is higher but in the same order of magnitude with our flux values found in rainwater. We can then conclude that the rains studied in this paper are not unusual events."

6) "Specific comments 1) P1, title, I feel that author can provide more suitable title for this manuscript which present original topics in this study more correctly. The word of "rain water" or "wet deposition" should be include, and they should avoid to use "solubility" (see general comment)."

The only interest of this paper is to present measured solubility in natural rainwater on Kerguelen Islands and so we cannot remove this paramount keyword from the title. For example, a paper published in GBC presenting similar data collected in other regions (Lim et al. 1994) is entitled "Solubility of Al, Pb, Cu and Zn in rain sampled in the marine environment over the North Atlantic Ocean and Mediterranean Sea". According to Reviewer#1, we changed the title including "rainwater": "Solubility of iron and other trace elements in rainwater collected on Kerguelen Islands (South Indian Ocean)".

7) "2) P6067, line 6-8. Authors described in the introduction that "Soluble iron in soil represent 0.5% of the total iron while it ranges from 0.1% to 90% in aerosols, rain and snows, sampled at different places and times". As authors indicate, many of laboratory experiment for investigating dust Fe solubility was conducted, the reported solubility range from the experiments is so wide. Part of this is due to experimental protocol for investigating the solubility. The protocol is adopted by aerosol Fe researcher, and

the operational definitions are so different among the researchers (differ in filtration method, pH for solution, etc.). This is one of compelling reason for explaining the wide range of reported solubility. Therefore, it is better to add a description of this point, additionally to other controlling factor for the wide reported range."

The reviewer is right, we added a description as suggested: "All of these factors combined together can explain the wide range of iron solubility values found in the literature. But, it has to be noted here that part of this range is also due to different experimental protocols used by different researchers for investigating the solubility, which hinder our understanding of the factors controlling solubility (e. g. Baker and Croot, 2010;Â ăWitt et al., 2010; Shi et al., 2012Â ă; Buck and Paytan, 2012Â ă; Morton et al., 2013)."

8) "3) How to clean PC filters? How much is the PC filter's diameter?"

You can find the description of the filter washing protocol page 5, lines 125-129: "The Nuclepore[®] PC filters (0.2 μm porosity, diameterÂ ă: 47 mm) were i) washed in a bath of 2 % v/v Romil-UpATM HCl for almost 2Â ăh under the ISOÂ ă1 laminar flow bench, then ii) rinsed with ultra pure water, iii) clipped with special rings (FilClip[®]), previously washed by the protocol for materials described above, and iv) stored individually in washed polystyrene Petri dishes until use." We added this part of sentence: "previously washed by the protocol for materials described above" to specify the washing of special rings. We added the information about the diameter of filters.

9) "4) It would be helpful for reader to add a schematic draw of rain collector funnel and filtration devise in Figure 2. This is very helpful for reader's understanding that how to collect the rain samples."

It is right. The description alone is difficult to understand how the sampling device is. We added a drawing of the collector on Figure 2 (Figure 2b), in addition with the picture (Figure 2a).

10) "5) I wonder that rain water samples can't pass 0.2 μm PC filter only by gravity

filtration. If rain water accumulate to upper part of the device on the filter, there was possibility of absorption of many particulate TM onto wall of the device and funnel. This can induce more high proportion of soluble fraction artificially. Did the rain water sample immediately pass the filter during rain event without any suck? I think schematic draw of the device helps for readers understanding in this point too."

The chosen filter is highly hydrophilic and helps water to pass through. We done laboratory blanks with ultra pure water to simulate a rain event and we tested a couple of filters using a commercial filtration device (Nalgene). For this last experiment that you can easily reproduce for your own, filter turns wet and water begins to flow spontaneously down after less than one minute even with only one or two millimeters of surrounding water. The flow-rate is about ten milliliters per minute. The Teflon walls surrounding the filter in the filtration part of the low density PE funnel bottom are vertical until filter and allow to prevent any particulate deposition on a flat section. We did not detect any suck problem as long as the water is poured slowly enough during blank experiments. For the sampling on Kerguelen Islands, we collected the sample after the end of rain events and we did not observe accumulation too. So, we think that no suck occur thank to the extremely low concentration of particulate material found in rain samples. This certainly will not be true with another filter type and with rains containing more suspended particulate material.

11) "6) Authors described in the text that soluble fraction of rain samples were collected into 500ml PP bottle, then stored in a 60 ml Teflon bottle, finally the samples were transferred into PE sampling vials. Then, authors only described that the sample was measured by HR-ICP-MS. Authors should add an information that how much time did it take to transfer the sample from 500 ml PP bottle to final PE vials. Which timing did the sample receive an acid for measuring TM by HR-ICP-MS? Was there no loss of TM by adsorption onto wall of bottles or vials before the measurement?"

We completed the text to provide supplementary information as asked (2.3): " Finally and less than half on hour after the collection of the sample, part of the soluble fraction

of rain was stored in a 60 mL Teflon$^{®}$ bottle. Teflon$^{®}$ bottles have undergone the same washing protocol as the 500 mL bottles. They contained enough Romil-UpATM HNO3 to give a 1% concentration of acid when filled with the collected rainǎ; the acid solution was used to prevent adsorption of trace metals into the Teflon$^{®}$ bottle walls during the storage of samples (between six months and two years) before trace metal analyses back in the laboratory." and 2.4 (first sentence): "Back in the laboratory and just before analyses, the soluble fractions of rains (stored in 60ǎmL 1% HNO3 acidified Teflon$^{®}$ bottles) were transferred into PP 15ǎmL sample vials that had been thoroughly washed (see Heimburger et al. (2012a) for details of the washing protocol)."

12) "Result and discussion Section 3.1 7) There should be a data Table with all the soluble and particulate TM concentrations together with the collected rain volume, time (period) for each rain event. These data Table can be placed either in the actual paper or in an electronic supplement. These data are available the reader may better be able to confirm the grate proportion of soluble fraction in the total fraction and the estimated deposition flux. Also, table for value of laboratory and field blank are available for readers to confirm Qi value in the text."

For the five non contaminated samples, we added Table 2 with sampling conditions and a supplementary reading table with soluble and insoluble concentrations. We do not wish to publish blank data because it is not useful for the reader. Nevertheless, we inserted all the measured quantities in all the blanks and samples in this document for reviewers and editor only. As stated above, contaminated samples should not be published because they are contaminated and related data could confuse readers. If we discuss about these samples at the beginning of this paper, it is to point out huge difficulties to obtain valuable rain samples in very remote areas and to explain how we have rejected its. This information would be useful to set up further field experiments.

13) "Section 3.2 8) Authors determine that three rain samples were free from local contamination by using definition of Ti/Al ratio. However, two of the Ti/Al ratio (rain

P1_10 and P3_08) are slightly over the range of the dust deposition (Figure 4). Under the authors criteria, may be these two rain sample were slightly influenced by soil Ti/Al ratio. I feel that authors should compare all 14 rain sample data more carefully, and present with additional persuasive evidence for discussing that the three of the rain samples were free from local contamination. See general comment."

As stated in the first paragraph of response to Reviewer#2, we have changed our criteria which is now based on soil composition only. This is more simple and we select two extra rainwater samples. The main issue of the previous Figure 4 criterion was the narrow plotted range of Ti/Al ratio in dust deposition samples. This range is calculated using two weeks integration period measurements over two years and do not reflect the full variation of this ratio on an event basis, so we cannot use it directly in Figure 4. Possible contamination by local soils remains a strong evidence for P6_09 to P5_08.

Now, we discuss on five rainwater samples. The addition of two extra samples has had no effects on the conclusions. Solubilities stay high, similar for all the considered five rain samples as they were for the three previously considered ones. The solubility median values of each element did not change. Solubility found in the locally contaminated samples is less than twice the one in kept samples, except for manganese which solubility remains high. We added a sentence paragraph 3.4: "In contrast, solubilities measured for the rejected rain samples show much lower values, for example with a median of 17% for Ti, 9% for Fe and 30% for Al."

14) "Section 3.3 9) P6076, line 1-3. Authors describe that "Measured rain fluxes are then consistent with the atmospheric total deposition fluxes. We can conclude that the rains studied in this paper are representative of average rain events on Kergeren Islands". I do not understand the meaning of this sentence. Why can they judged their observed rains were representative of average rain event of Kergelen Islands? Reader need more explanation."

We removed the expression "average rain event" and we give a better explanation on

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our calculation of flux "per event".

15) ""10) Authors compare mean calculated value of Al and Fe in both wet and total fluxes in discussion (section 3.3). However, comparison of mean values are not suitable for this evaluation. See general comment."

See response to the "general comment 3)", we have rewritten this paragraph.

16) "Section 3.4 11) Author can compare their data (proportion of soluble fraction) to previous studies data from other regions. Also they can compare their data to experimental solubility data from other oceanic and coastal regions, which including fine and coarse dust particulate from many kind of sources (e.g. Hanson et al., 2001; Hsu et al., 2005; Wu et al 2007; Ooki et al., 2009; Schroth et al., 2009), and rain and cloud water (Kieber et al., 2001; 2003; Mackie et al., 2005; Fan et al., 2006)."

Our purpose is not to present a review on rain solubilities, which is already well done by e.g. Mahowald et al. 2005 or Fan et al. 2006. We discuss in paragraph "3.4 Solubilities" on relevant values, which demonstrate that very high solubilities can be found far from continental sources over oceanic areas or in Antarctica.

17) "12) Back trajectory and wind roses data for all 14 rain samples are helpful for discussion. These data should be present in the manuscript text and figures. See general comment."

We would not provide information on the possible contaminated rains; we think that this information can disturb future readers.

Back trajectories are not useful in a figure here because none of them reveals continental sources but they show air masses traveling over ocean from West to East during several days.

The sampling period of each event was short and wind did not change its direction during sampling of a rain. A graphical representation as wind rose is thus not necessary, we put instead wind direction for each kept event in Table 2.

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Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/10/C2915/2013/bgd-10-C2915-2013-supplement.pdf