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

Anonymous Referee #2

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Journal: BG Title: Solubility of iron and other trace elements over the Southern Indian Ocean. Author(s): A. Heimburger et al. MS No.: bg-2013-112 MS Type: Research Article

This manuscript reports results of measurements of soluble, and particulate trace metals (TM : Al, Ce, Fe, La, Mn, Nd, Ti) concentrations in rain samples which were collected at Kerguelen Archipelago in the Southern Indian Ocean. Authors report TM deposition flux by each rain event, and indicate that high proportion (generally greater than 70%) of total fraction in the rain water were comprised by soluble fraction, except for Ti. Authors conclude that long distance transport and chemical processes are important for understanding the high soluble proportion of TM concentrations in rain water, and also suggest that the solubility should be re-evaluated for estimating soluble

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TM deposition flux for remote oceanic region by current atmospheric models.

Over all, this topic "quantitative evaluation of wet atmospheric TM deposition" is precious information for the wide chemical oceanographic community. Several TM, especially Fe, studies estimating total deposition were already reported by Author's previous studies (Heimburger et al., 2012, GBC; Heimburger et al., GBC, accepted manuscript) and other research group's previous studies (e.g. Fung et al., 2000, Arimoto et al., 2003; Mahowald et al., 2009). However, data for estimating wet depositions for TM in the oceanic area from direct observation is very scarcity (Colin et al., 1990; Guieu et al., 1997; Kieber et al., 2001; 2003; Mackie et al., 2005; Fan et al., 2006). In this aspect, I agree that the reported data in this manuscript is important for estimating TM wet deposition flux in the ocean. However, there are several major issues that need to be addressed before this paper can be considered for publication.

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. 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

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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).

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%=ãĂŤXãĂŢsoluble/ãĂŤXãĂŢtotal. 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.

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). 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 (ug m-2day-1) is different from the unit for wet deposition (ug 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

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contribution of wet deposition to total deposition flux. Then, authors can compare the wet/total deposition flux among each field campaign.

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).

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.

3) How to clean PC filters? How much is the PC filter’s diameter?

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.

5) I wonder that rain water samples can’t pass 0.2um 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

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of the device helps for readers understanding in this point too.

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?

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.

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.

Section 3.3

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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 Kergeren Islands? Reader need more explanation.

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.

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).

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.

End of review

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