Interactive comment on “Chemical characterisation of iron in Dust and Biomass burning aerosols during AMMA-SOP0/DABEX: implication on iron solubility” by R. Paris et al.

Anonymous Referee #1

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This manuscript presents some very interesting results on the solubility of iron contained in dust and biomass burning aerosols collected over West Africa. The measurements of iron solubility are well supported by other chemical measurements, which help to characterise the aerosols examined and offer the possibility to try to examine potential influences on iron solubility. The important findings, as I see it, are that the iron contained in those aerosols comes from mineral dust (even in the biomass burning aerosols), that the fractional solubility of iron in the biomass burning aerosols is generally higher than in the dust aerosols, and that the dust aerosol is externally mixed with biomass burning aerosols. These results present some interesting problems in interpreting the dataset that I think could be explored more fully. On P 25033 l 11 the authors state that “mixing [of dust] with combustion particles enables the increase of iron solubility”. How can this process take place if the dust and combustion aerosols are externally mixed, as stated? If they are externally mixed, they are not in contact with one another. Uptake of gaseous species onto dust, once it is mixed with a biomass burning plume might have some effect on iron solubility in the dust, but this might be difficult to confirm (unless perhaps the electron microscopy results of Chou et al., 2008 show evidence for the presence of S and N on dust particles?). Alternatively, the effect might be an artefact of the experimental method used to determine iron solubility in the samples (subjecting the samples to ultrasonication in aqueous solution), which is the equivalent of internally mixing the aerosol components, and thus actually allowing the dust and biomass burning particles to interact. I don’t think that it is possible to state with absolute certainty that, if it were possible to remove only the dust particles from the biomass burning samples and then determine their fractional iron solubility, that the results would have been the same as those presented in the manuscript. From the methods section and a few vague statements in the Results and Discussion section it is clear that the authors have available comparable data on the solubility of several other elements besides iron for this dataset. I am rather disappointed that they have chosen not to present that data properly in this manuscript. Certainly the solubility of iron is the major topic of interest from this dataset, and it is right that this should be the major focus of the manuscript, but there is also much to be learnt about the controls on iron solubility from the behaviour of other elements. Just as one example, several studies have implicated redox changes as being significant in enhancing iron solubility during atmospheric transport. Comparison to the behaviour of a non-redox active element (e.g. aluminium) might help to highlight the importance of this process.

Other Comments The use of ultrasonication to remove soluble components from aerosol samples has potential problems for elements, including Fe, that are redox active. Ultrasonication produces acoustic cavitation and this results in the formation species such as H2O2 (Kanthale et al., 2008), which can reduce insoluble Fe(III) to soluble Fe(II) and thus alter Fe solubility.
Are the two biomass burning groups BB1 and BB2 in any way related to the aged and fresh BB referred to by Formenti et al., 2008.

P 25029, l 22. It seems a little odd that the Fe content of the dust samples is lower than those of the BB samples. Are these differences really statistically significant?

P 25030, l 13. “30% of Fe data unusable”. Please explain exactly what data are included in Table 2. Do the average and min values quoted for soluble Fe concentrations only apply to the 70% of samples above detection limit? If so, the comparison between soluble Fe values for BB and DUST samples is potentially misleading. It would be helpful to have limits of detection for soluble Fe and oxalate (if not all other analytes as well) presented in the manuscript.

P 25030, l 15. “Soluble fractions of ... terrigeneous origin ... are similar in all samples”. Does this mean that the fractional solubilities of all these elements are \( \sim 1-2\% \) (as shown for Fe in Fig 3), or that for each element the fractional solubilities in the DUST and BB samples are similar? If the former, this would be a surprising result, as other studies have shown significant differences for the fractional solubilities of some of these elements in aerosols (e.g. Baker et al., 2006).

P 25030, l 25. The statement made here about changing K/S in ageing biomass burning aerosol is interesting, but there is no follow-up statement regarding its relevance to the dataset examined here. Are there differences in Kexc/S in your dataset, perhaps between the BB1 and BB2 groups?

P 25032, l 20. Please explain what the SEVIRI dust observations are. There is no reference to this anywhere else in the manuscript.

P 25033, l 2. The statement that “soluble iron for BB filters appears to be higher by 2 orders of magnitude than the DUST filters (Fig. 3)” is surely wrong. Figure 3 shows median Fe solubility for DUST samples of 0.9% and for BB samples \( \sim 2\% \). Thus the difference is approximately a factor of 2, not 2 orders of magnitude.

P 25033, l 24-27. This statement regarding the relative solubilities of Fe in the two BB groups seems to be stretching the data a little far. The difference in median solubilities between the two groups is only 0.2%, when both groups have a range of solubilities covering more than 10 times this difference. A firm statistical analysis is required to confirm this statement.

P 25034, l 12-18. It seems strange to me that the Conclusions section should finish with discussion of data on soluble P concentrations that was not covered in the Results and Discussion. These data are useful and interesting. Please present them properly, along with the solubilities of other elements than Fe.

Table 1. It would be useful to indicate in the table the samples for which Fe solubility was determined.

Figure 3. Please add the number of samples in each category used to produce the boxplot here.

Figure 4. It appears that the two data points closest to the origin on this graph are plotted as orange circles AND as blue dots, and that they have therefore been included in both regression equations shown. This cannot possibly be justified, since the caption implies that there are two separate mineralogies in these dust samples. Those two samples cannot belong to both groups.

Error bars should be shown on Figures 2 and 4, especially for the calculated parameters Kexc, %SFe and %SMg. It would also be appropriate to give an indication of the uncertainties in the measured parameters in the Methods section.

Kanthale, P., Ashokkumar, M., and Grieser, F.: Sonoluminescence, sonochemistry (H2O2 yield) and bubble dynamics: Frequency and power effects, Ultrasonics Sonochemistry, 15, 143-150, 2008.

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