

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.

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We would like to thank the two anonymous referees for their careful reading and thoughtful comments. We respond to the comments of each referee separately. Their comments are included in italic, followed by our responses. Since some of the referees have some of the same comments, we repeat our responses.

Anonymous Referee #1

On P 25033 I 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?

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RP: Even if the study of Chou et al. (2008) emphasize external mixing between dust and BB particles in the ambient atmosphere in the region of Sahel, recent publication of Hand et al. (2010) emphasize an internal mixing when dust are directly observed in biomass burning plume. Thus, we added and modified the discussion in considering this new information. p7 L2: I added "in part possibly internally mixed (Hand et al., 2010)" p12 L24: I added "Nevertheless, our results show the solubility of the iron contained within dust is enhanced due to the internal mixing between dust and BB particles"

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. Comparison to the behaviour of a non-redox active element might help to highlight the importance of this process.

RP: We added a discussion on the behaviour of terrigenous elements and iron about redox state as proposed. p12 L14-17: I added "However, the increase of solubility in BB samples is also observed for the terrigenous elements which are non-redox active (see above). Consequently, a change of oxidation state of iron is probably not significant in enhancing iron solubility in mixed samples."

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.

RP: I agree that ultrasonication could produce species such as H₂O₂, but my hypothesis is that this artefact is compensated by the fact that H₂O₂ can oxidize soluble Fe(II) to insoluble Fe(III) (Zuo et al., 2005, Pehkonen et al., 1993). Change of soluble iron concentrations by the method could be as negative as positive. Also, the dissolution enhancement of non-redox elements confirms this hypothesis. p12 L14-17: I added

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"However, the increase of solubility in BB samples is also observed for the terrigenous elements which are non-redox active (see above). Consequently, a change of oxidation state of iron is probably not significant in enhancing iron solubility in mixed samples." Moreover, our results are consistent with values found in the literature about the solubility of Fe in dust particles (Baker et al., 2006; Bonnet and Guieu, 2004; Johansen et al., 2000).

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.

RP: The biomass burning groups are not related to the aged and fresh BB referred to by Formenti et al., 2008. The group BB1 is composed by Old BB and Smoke Haze, the BB2 by Old BB and Fresh BB. We didn't find any correlation between the air masses age and the state of mixing between dust and biomass burning. p8 L9-11: I added "If we compare our group samples BB1 and BB2 to Formenti et al., 2008, there is no correlation with the aged and fresh biomass burning samples, so the precedent hypothesis shouldn't be the good one." Given that dust is the only provider of iron, we decided to base our study on state of mixing, rather than age of BB air masses.

P 25029, I 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?

RP: Taking into consideration the figures, it is clear that there are not statistically different. Fe content in the 3 groups is significantly the same considering the standard deviation, which is consistent with the dust origin of iron. p7 L15: "5.5% (+/- 0.5%); 5.4% (+/- 0.4%) and 5.1% (+/- 0.3%) respectively"

P 25030, I 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 the other analytes

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as well) presented in the manuscript.

RP: Indeed, due to the number of samples under detection limits, we changed the data in Table 2 and we presented the median concentrations of dissolved species. Detection limits for iron and other elements are presented in details in the referenced works (Sofikitis et al., 2004 and Desboeufs et al., 2003) (P 25027, I 23-25) and correspond to dissolved concentrations (ppb). In the case of this paper, the concentrations are presented in $\mu\text{g}/\text{m}^3$ (since we work on aerosol filters) and hence depend on the sampled air volume. Thus, the detection limits depend also of the air volume for each filter.

P 25030, I 15. "Soluble fractions of ... terrigenous origin ... are similar in all samples". Does this mean that the fractional solubilities of all these elements are ~ 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).

RP: The sentence "Soluble fractions ... of terrigenous origin ... are similar in all samples" means that for each element the fractional solubilities in the DUST and BB samples are similar. This sentence has been changed to be clearer by "The soluble fractions of typical elements of terrigenous origin (Al, Fe, Si, and Ti) are lower in DUST samples than in BB samples, but always with values inferior to 3%.". It has been also moved at the end of paragraph since it was not at the right place in the discussion. Moreover, we added a discussion on the behaviour of terrigenous elements and iron about redox state as proposed. p12 L14-17: I added "However, the increase of solubility in BB samples is also observed for the terrigenous elements which are non-redox active (see above). Consequently, a change of oxidation state of iron is probably not significant in enhancing iron solubility in mixed samples."

P 25030, I 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

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the dataset examined here. Are there differences in Kexc/S in your dataset, perhaps between the BB1 and BB2 groups?

RP: As mentioned above, the group BB1 and BB2 are not dependent on the age of biomass burning plumes, but a mixing state. In consequence, it was difficult to follow-up the data K/S and oxalate formation as a function of ageing aerosol.

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

RP: We added the reference of SEVIRI website in the manuscript (http://radagast.nerc-essc.ac.uk/Data.htm#SEVIRI_data) (P 25032, I 20) SEVIRI is a 50 cm-diameter aperture, line by line scanning radiometer, which provides image data in four Visible and Near-InfraRed (VNIR) channels and eight InfraRed (IR) channels.)

P 25033, I 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 ~2%. Thus the difference is approximately a factor of 2, not 2 orders of magnitude.

RP: Indeed the difference is approximately a factor of 2, not 2 orders of magnitude. We changed it in the text

P 25033, I 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.

RP: Actually, the difference in the relative solubility of Fe in the two BB groups is not significantly different. So we modify the text and change "lowest" by "same".

P 25034, I 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

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and Discussion. These data are useful and interesting. Please present them properly, along with the solubilities of other elements than Fe.

RP: See table 2: 2 times more soluble P in BB samples, but the results with the PIXE method didn't allow us to calculate more precisely the solubility of this important nutrient.

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

RP: I added the samples and the group for which SFe was determined in the Table 1.

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

RP: I added the number of samples.

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.

RP: I included the two data points, close to the origin, in both regression equations because to my opinion they belong probably to both groups. If the first regression equation (slope 8) corresponds to Fe from illite and the second one (slope 38) to Fe from another clay, I suppose that soluble Fe in these 2 samples is issued from both two minerals in the samples. On the contrary, for the other samples, the soluble Fe is mainly released from illite or the other clay. I clarified this assumption by adding in the legend of Figure 4: “We supposed that the 2 points the closest to the origin belong to both regression equations on the assumption that there is not only one predominant mineral as SFe provider”.

Error bars should be shown on Figures 2 and 4, especially for the calculated parame-

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ters Kexc, %SFe and %SMg. It would also be appropriate to give an indication of the uncertainties in the measured parameters in the Methods section.

R.P.: I added the error bars

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	BB			DUST		
	median	min	max	median	min	max
Al	0.13	<DL	0.48	0.21	<DL	0.95
Ca	4.27	<DL	12.52	5.21	0.45	16.79
Fe	0.10	<DL	0.43	0.07	0.01	0.55
K	2.16	<DL	4.28	0.83	<DL	3.2
P	0.16	<DL	0.18	0.10	<DL	0.12
SO ₄ ²⁻	4.12	<DL	5.41	2.08	<DL	4.09
NO ₃ ⁻	4.85	<DL	7.42	1.60	<DL	4.54
C ₂ O ₄ ²⁻	1.07	<DL	1.44	<DL	<DL	<DL

Table 2

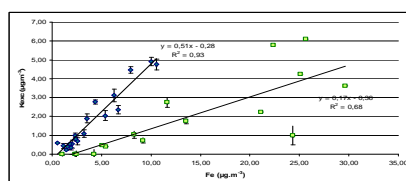


Figure 2

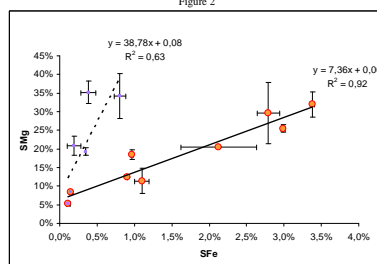


Figure 4.

Fig. 1.

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