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Interactive comment on "Dry season aerosol iron solubility in tropical northern Australia" *by* V. H. L. Winton et al.

Anonymous Referee #2

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This manuscript reports the results of a study of aerosol and gas composition at Gunn Point, Northern Territories, Australia, during a period in the dry season that was periodically impacted by biomass burning events. A large amount of good quality data appears to have been generated and the subject of the manuscript – the impact of biomass burning on aerosol trace metal solubility – is one that is relevant to the journal. However, the manuscript suffers from a number of problems and will require major revisions before it is suitable for publication. Currently the text is marred by inaccuracy, inconsistency, vagueness and lacks focus. It does not do justice to a worthwhile and interesting study. I only list my major concerns here, but I would hope that the authors would submit a much more self-consistent and concise revised manuscript.

Accuracy: "During dust event "A" fractional Fe solubility peaked at 12%" (page 10, line 23 and repeated on page 12 and 16). According to Figure 6, the upper limit of fractional

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Fe solubility during event “A” was ~8%. On the figure the 12% value corresponds to burning event “E”. Which is correct, the figure or the text?

“This same set of total trace elements (Cr, As, Mo, and V) also peaked on the 9 June during fire event “E” (Fig. 5).” This statement also does not stand up to scrutiny. Of the elements listed, only As has a (slightly) higher concentration in the sample associated with event “E” than in the previous sample. The data referred to is presented in Figures 3 & 4, not 5.

I would urge the authors to be much more cautious in their use and interpretation of enrichment factors. There are many pitfalls associated with their use (including the choice of reference material and reference element, and whether the reference material is actually representative of mineral dust in the atmosphere – see Reimann and De Caritat (2000) and Arimoto et al. (1989) for brief descriptions of some of these pitfalls). In light of these problems, most authors choose to use much higher values of EF to describe individual samples as “enriched”, e.g. >5-10 (e.g. Duce et al., 1983; Gelado-Caballero et al., 2012). The values of EF presented in Table 3 are almost all rather low (there is only one value above 10) and therefore the case for describing most elements as enriched is weak. The author’s attempts to link these low values to potential anthropogenic emission sources several thousand kilometres distant from their sampling site (e.g. in Brisbane) are untenable (even without considering the uncertainties in the air mass back trajectories used to make the link).

The value for dry deposition velocity of Fe used here has been taken from Duce et al. (1991) and Baker et al., (2003) – see page 8. These authors estimated the uncertainty in dry deposition velocities to be a factor of 2-3. Here the uncertainty in this parameter is estimated to be +/- 50% (footnote to Table 2). How do the authors justify this?

“biomass burning contributes around 60-70 % of the total soluble Fe deposition, where the dust contribution is less (40-50 %)” (page 14). On the face of it, these numbers don’t add up.

Consistency: Interpretation of the manuscript would be easier if the air mass types encountered during the campaign were identified in a consistent manner. I was extremely puzzled by the apparent contradiction of the statement “No trajectories fell in the ‘mainly oceanic’ category” and the labelling on Figures 3-6 of a period of “Marine conditions”. Only on page 13 does it become clear that “marine conditions” actually corresponds to type b (coastal, moderate urban/industrial activity), as defined on page 7. Understanding of the influence of air mass source would also be improved if the periods influenced by each identified type were marked on those figures.

It would be helpful if the way that details of the many measurement and analysis techniques presented here could be harmonised as much as possible, especially for the two types of aerosol collection. Were the quartz filters really handled in a trace metal clean laboratory?

On page 11 trajectory type c is described as including “major cities and industrial areas in Brisbane”. On page 12 the same trajectory type is described as “times when the air mass passed over central Australian desert and low population areas of inland Australia”.

Vagueness: Section 3.4 is good example of this (but there are several others). This manuscript is based on a rich multi-parameter dataset. Surely the authors can find more scientific descriptions than “x was high at the same time as y”.

“annual dry season” (page 4 & 14). What does this mean?

Focus: The title of the manuscript indicates a study focussed on aerosol iron solubility. I think some of the discussion of peripheral parameters could be removed without any risk of degrading the manuscript. As an example, the potential source of As from volcanoes in these samples (page 13) is of very little relevance. On the other hand, it is quite possible that the fractional solubility data for the other trace metals measured during the campaign could prove to be very informative. There is a little discussion of this for Al, Ti and Mn, but the actual data are not shown. Apparently the trends in

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fractional solubility variation over the campaign are not unique to Fe. Does this imply that the factors that regulate Fe solubility in these samples also regulate the solubility of Al and Ti? What about the other trace elements? Please add a plot of fractional solubility over time (similar to Figures 3 – 6) for all the elements possible, even if this has to be put in the Supplement.

There are some lines of discussion that I feel have been left incomplete, especially in relation to the influence of biomass burning on the results obtained. Apparently (page 8) the nss-K/Fe ratio during fire events was higher than at other times. Since nss-K is a well-established marker for biomass burning, does that result imply that biomass burning is an insignificant source of Fe to the aerosol? The answer would depend on the emission ratios for K and Fe from biomass burning. There are numerous laboratory-based studies of biomass burning emissions. Please could K/Fe ratios for such studies be added as a comparison. In a similar vein, on page 11 the authors state that enrichment factors for Fe were between 0.9 and 1.3 and that therefore "anthropogenic pollution was not a dominant source of Fe to Gunn Point". What implications does this result have for biomass burning as a source of Fe? Perhaps it implies that biomass burning is also relatively unimportant, but perhaps not. Entrainment of fine soil particles into flames and smoke plumes could add Fe to the aerosol without affecting enrichment factors. Again, emission factors from laboratory studies could be informative here, at least with regard to direct emission from combusted biomass. Although the study of Guieu et al. (2005) on biomass burning-related emission of Fe in the Mediterranean is cited several times, I would like to see the authors make a direct comparison between the results of the two studies. Are they consistent with one another?

Authorship: There is absolutely no need for the authors to refer to themselves through the use of Personal Communications. All of these instances should be removed.

Citations: Please update the citations of Fomba et al, ACPD, 2012 and Ito & Shi, ACPD, 2016 to their final published forms in ACP (2013 and 2016 respectively).

Methodology: Filtration of water soluble trace metal leachates. The authors only state that one sample (GP22) was filtered through 0.2 um filters after leaching (page 5) and that leachates (the non-0.2 um filtered leachates or also the filtered leachate of GP22?) contained visible particles after settling (page 14). If leachates contained particles, what efforts were made to disperse these within the solution immediately prior to analysis by ICP-MS?

Were quartz filters washed before use? If so, how?

Please give a little more detail on the method used to determine total metal concentrations, e.g. which acids were used for digestion.

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