

Author response to referee #2

We thank the reviewer for their time and constructive comments for improving this manuscript. We have reproduced the reviewer comments below and have appended our responses to each of their queries in italics. Technical revisions and minor changes were highly appreciated and were followed as suggested. We have only reproduced the additional comments in the referee's supplement if rephrasing of entire sentences and additional data was requested or in a very few cases where we disagreed with the suggestions. Page numbers refer to the revised version of the manuscript.

Anonymous Referee #2 interactive comment

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 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?

Comment: The text is correct but the fractional Fe solubility data in Fig. 6 was wrongly plotted. The fractional Fe solubility in dust event "A" is 12 %. Fig. 6 has been replotted with the correct fractional Fe solubility data. The data in all plots have consequently been checked.

"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.

Comment: Total As and Pb have higher concentrations during fire event "E" (Fig. 4). The text has been re-written on page 9, line 26-28.

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; GeladoCaballero 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).

Comment: We agree with referee #2 and note the limitations of using enrichment factors (EF) in page 11, lines 25-27 and include the references suggested (Arimoto et al., 1989; Reimann and Caritat, 2000). We follow the Duce et al. (1983); Gelado-Caballero et al. (2012) classification of EF, i.e., "enriched EFs" between 5 and 10 and "low EF" less than 5. Following this, we have modified our interpretation of the EFs in page 11, lines 27-30. This

suggests that the origin of the material is similar to the upper continental crust for all elements except Pb (GP19) and Cr (GP9) which have EFs greater than 5. As the new classification of EFs discounts potential anthropogenic emission sources, we have deleted the discussion concerning enriched elements of Cr, Mn, Pb, K, As, Mo and V.

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?

Comment: To be consistent, we have used the uncertainty of dry deposition velocities (a factor of 2-3) reported in Duce et al. (1991); Baker et al. (2003). This had been updated on page 10, lines 18-19 and in Table 2.

“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.

Comment: The sentence has been re-written on page 3, line 14-16.

“Ito (2015) shows that biomass burning derived soluble Fe contributes substantial inputs of soluble Fe to tropical and Southern Ocean waters downwind of Australia.”

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.

Comment: Air mass types are now referred to consistently throughout the manuscript. The reference to “mainly oceanic” trajectories has been deleted (page 8, line 4) as it is irrelevant, i.e., no trajectories were solely over the ocean during the campaign.

“marine conditions” are now referred to as “coastal conditions.”

“Marine conditions” in Figs. 3-6 have been renamed “coastal conditions” to be consistent with the air mass trajectory during that period - type b) “coastal, moderate urban/industrial activity” (Fig. 1b).

The heading “4.5.2. Anthropogenic and sea spray sources in marine conditions” has been renamed “4.5.2. Sea spray sources during coastal conditions”.

In Figs. 3-6 we have added the trajectory types to the labels highlighting the periods of dust events, biomass burning events and coastal conditions.

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?

Comment: We have rearranged the methodology by putting information for each type of filter (quartz and Whatman 41) under the relevant headings. For the blank filters, we have stated which type of blank is associated with which type of measurement (page 4, lines 25-32). The quartz filters were analysed at CSIRO Ocean and Atmosphere and this is now clear. The section about sample preparation for trace metal work has been moved to the heading “2.3. Trace element analysis” (page 5, lines 2-5).

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”.

Comment: For consistency, we have changed the name for trajectory type “c” to “inland, major urban/industrial activity.” This has been updated in the Fig. 1 caption and throughout the manuscript. Dust events are associated with trajectories that passed over central Australian desert (page 12, lines 6-8). “and low population areas of inland Australia” has been deleted from the sentence as the trajectories also passed over major urban/industrial regions in Sydney and Adelaide.

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”.

Comment: Section 3.4 has been rewritten.

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

Comment: In northern Australia, the dry season ranges from May/June (early dry season) to October-November (late dry season) (Andersen et al., 2005). We have deleted “annual” and defined the dry season on page 3, lines 22-23.

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 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.

Comment: We agree with referee #2 and have removed discussion around peripheral anthropogenic parameters, such as As, Mo and Cr on page 11 from lines 27. “Anthropogenic” has been removed from the heading 4.5.2 which now focusses on coastal conditions. The heading has been renamed to “4.5.2. Sea spray sources during coastal conditions.”

Regarding the fractional Fe solubility of other trace metals, we have added plots of fractional solubility of Al, Ti and Mn in Fig. 6. The temporal variability of fractional Al and Ti is similar to Fe, i.e., fractional solubility of Al, Ti and Fe were highest between 4 and 20 June and suddenly dropped after 20 June during the largest and most proximal fires (as discussed on

page 11, lines 4-11). On the other hand, Mn is relatively soluble and appears unrelated to the fractional solubility of Fe, Al, Ti. As far as we are aware no data for these elements has been collected at biomass burning source regions during the dry season. Thus, we cannot speculate that the factors that regulate Fe solubility in these samples may also regulate the fractional solubility of Al and Ti but not Mn. We have eluded to this on page 16, lines 11-16 and suggest future work should investigate these elements in conjunction.

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?

Comment: More studies are required to determine the influence of biomass burning on soluble iron both at the source and in long range air masses downwind of biomass burning sources. In terms of the influence of biomass burning in this study, we have tried to focus the discussion, conclusion and abstract around the following:

During the large burning events in this study, fresh elemental carbon seems to be an insignificant source of Fe to the aerosol (it has a low Fe solubility, it is initially hydrophobic and contains relatively little Fe). We have already pointed this out on page 13, lines 1-2 “During these fire events, total PM₁₀ Fe and soluble Fe concentrations and fractional Fe solubility (~3 %) were considerably less than the average concentration and fractional solubility throughout the campaign.” However, biomass burning may be important through indirect processes such as oxalate modification, as a substrate to transport long range aerosol Fe, and through the entrainment of fine soil into the plume. The nss-K/Fe ratio and the EFs for Fe in the plumes suggest that elemental carbon is relatively unimportant. Biomass burning could be important indirectly via soil entrainment into the smoke plume. We have already discussed the process of how Fe can be incorporated into biomass burning plumes on page 13, line 29-32. The values of the nss-K/Fe ratios and the EF could be explained by the process. We have added this to the discussion on page 11, lines 31-32 and page 13, lines 21-24.

There are many papers that give emission factors for K (Gaudichet et al., 1995; Akagi et al., 2011) however, we are not aware of any that give emission factors of Fe from fires. Iron is not included in Akagi 's review.

Nss-K/Fe ratios for other studies have been added on page 8, lines 24-26 for comparison to our results (Paris et al., 2010;Srinivas et al., 2012).

We have made a comparison to the Guieu et al. (2005) study on biomass burning-related emission of Fe in the Mediterranean on page 16, lines 6-9. While the studies are not directly comparable, both suggest that biomass burning is not a major source of soluble iron to the ocean.

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.

Comment: References of personal communications have been removed and updated with published or submitted papers.

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).

Comment: Citations have been updated.

Methodology: Filtration of water soluble trace metal leachates. The authors only state that one sample (GP22) was filtered through 0.2 μm filters after leaching (page 5) and that leachates (the non-0.2 μm 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?

Comment: The instantaneous soluble iron fraction from these fine particles was leached into solution during the flow through leach. To avoid sucking fine particles into the ICP-MS, the leachates were left to settle in centrifuge tubes overnight before analysis. For total iron measurements, concentrated HNO_3 and HF were used to digest aerosol particles into solution.

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

Comment: The quartz filters were not washed. Pall tissue quartz filters are extremely low in soluble ion and carbohydrate blank concentrations. The oxalate blank, calculated using average collection volume of 1575 m^3 , is 0.0009 $\mu\text{g m}^{-3}$ with a MDL of 0.0002. Levoglucosan has no detectable blank with a MDL of 0.00002 $\mu\text{g m}^{-3}$. These blank concentrations have been added in page 7, lines 12-14.

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

Comment: All information for filter digestions can be found in Winton et al. (2016). We have added the acids (HNO_3 and HF) used in the digestion on page 5, line 30.

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