Manuscript: ACP-2016-419

Author response to referee #3

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 #3 interactive comment

Methodology

P5L11 "following the ultra-clean methodology" … is this a reference to a specific methodology?

Comment: We had added a reference for trace metal clean practices on page 5, lines 3-4:

"following trace metal clean practices (e.g. Cutter et al., 2010)."

Section 2.3.1 From what I understand, there are a number of published methods for determining iron solubility, and a number of operational definitions of iron solubility. How does the strategy presented here fit within the literature/precedent on this topic? Specifically, in P6L1, what does "Leaches 5–etc. were estimated" mean? Finally, why was GP22 in particular chosen for filtration?

Comment: Yes, there are a vast number of methods employed in the literature for estimating soluble iron concentrations of aerosols. These range from water soluble leaching methods (e.g. Buck et al., 2006), weak acid leaching methods (e.g. Shi et al., 2011;Baker et al., 2006), seawater leaching methods (e.g. Aguilar-Islas et al., 2010) to iron speciation methods (e.g. Spolaor et al., 2012;Chen and Siefert, 2004). The leaching methods vary in the leaching solution, volume and time (instantaneous to months). This variability gives rise to a number of operational definitions of soluble iron, and makes comparisons of results from different studies difficult. Although, there are few estimates of soluble iron in Australian dust and aerosols, for consistency, we use the instantaneous water leaching scheme that has previously been used for other studies of Australian aerosols (Winton et al., 2015;Winton et al., 2016). We have added the justification for using the instantaneous water soluble method on page 5, lines 7-11.

Due to the time and cost of analysing 20 leachates per sample, we only collected and analysed leaches 1-4, 6, 10 and 20. It has been widely reported in the literature that soluble iron concentrations exponentially decrease with subsequent leaches (e.g. Aguilar-Islas et al., 2010). We therefore, estimated the concentrations of the unanalysed leachates by fitting a power law curve to the soluble iron concentrations of leaches 1-4, 6, 10 and 20. "Leaches 5–etc. were estimated" has been rewritten as "Concentrations of leachates." We have clarified this on page 5, lines 11-18 and 20-23.

GP22 was chosen because it was particularly high in of soluble iron. This has been added on page 5, line 24.

P7L17 Is this the correct baking temperature?

Comment: The quartz filters were baked at 600°C and this has been corrected on page 7, line 8.

Results

P8L13 How is nss-K (i.e. versus total K) determined here? Is the assumption that all K is nss-K, since no trajectories were "mainly oceanic" (P8L1)?

Comment: The nss-K fraction of total K was obtained by subtracting the contribution of sea salt derived K from the measured K concentrations:

$nss\text{-}K = K - 0.037 \times Na$

where Na and K are the measured concentrations in aerosol samples and 0.037 is the K/Na ratio in sea-salt (Keene et al., 1986).

We have added this on page 6, lines 7-10.

P8L22 The nss-K/Fe ratio during non-fire events (1.3) is higher than that quoted for both crustal aerosol and polluted aerosol. What is the overall significance of this comparison?

Comment: The higher ratio for non-fire events suggests that even during the non-biomass burning events, biomass burning was still a contributing source of aerosol Fe. We have added this significance on page 8, lines 30-31.

P8L29 This discussion could benefit from some reference to the literature.

Comment: The exponential decrease of soluble Fe in sequential leaches is discussed on page 5, lines 11-12 and page, 9 lines 4-8 with reference to other studies who also observed this trend (e.g. Aguilar-Islas et al., 2010;Wu et al., 2007;Fishwick et al., 2014).

P9L1 Would you expect the same behaviour for samples collected under different conditions (i.e. during non-fire events)? And, what is the overall significance of this observation?

Comment: Yes, the proportion of soluble iron in <0.2 µm pool is likely to change between seasons as different sources (with different particle size distributions) turn on and off. For example, biomass burning has a finer particle size distribution to mineral dust. This has been discussed in the discussion concerning particle sizes and bio-availability on page 14, lines 17-19.

Section 3.4 These results could be presented more clearly—the correlations described aren't actually shown in the figures, and the figures are discussed out of order. Also, Na seems to be repeated in Figures 3 and 4. As a minor note, the section seems to be mis-titled, as it also includes discussion of elements other than iron. More importantly, I'm confused by the reference to "marine conditions" here, as earlier in the paper it was stated that no trajectories were mainly oceanic.

Comment: Section 3.4 has been rewritten. The figures are now discussed in order. Scatterplots showing the correlations have been added in the supplement (Fig. S3). Section 3.4 has been *retitled "Trace element mass concentrations". Na was repeated in Fig. 4 so the reader could see he high concentrations of total As, Cr and Mo during the marine conditions. We have deleted the Na plot from Fig. 4. "marine conditions" are now referred to as "coastal conditions" to be consistent with the air mass trajectory during that period - type b) "coastal, moderate urban/industrial activity" (Fig. 1b).*

Discussion

P9L29 I'm wondering about the first line of Section 4.1—technically, isn't the non-fire PM10 Fe concentration also similar to the Brazilian fire aerosol studies, given that there isn't an obvious correlation between PM10 Fe and fire event presence/absence? Is this a useful comparison? Also, according to Figure 3, the maximum PM10 Fe concentration actually appears to be ~0.8 ug/m3? In addition, what is the overall significance of the comparisons to other fire events if the results aren't scaled to total PM10 / some proxy for proximity to the actual fires?

Comment: Yes, the total Fe concentrations throughout the campaign are similar to the Brazilian fires. We have replaced "during fire events" with "during the campaign" on page 13, line 6. The maximum total Fe concentration throughout the campaign was 1.2 µg m^{-3} and the highest total Fe concentration for fire events was 0.82 µg m^{-3}. The Alta Floresta, Amazon Forest, Brazil is at a similar latitude to the Gunn Point site. As far as we know, there are no other estimates of total Fe concentrations in biomass burning aerosols in Australia, thus we have compared our results to other studies from tropical regions that experience seasonal biomass burning (e.g. the Alta Floresta) and the open ocean. In tropical regions, it is interesting that the concentrations of total Fe are similar at the source (Gunn Point and Alta Floresta) but decrease over the open ocean (Atlantic). We have rearranged the section 4.1 to make this clearer.

Section 4.3 I find this discussion confusing as written and very difficult to follow. In particular, I'm confused by this statement: "These estimates are similar to dust estimates around 0.5-2 % at relatively high Fe mass concentrations." Perhaps it might make sense to merge this section with the discussion of the fire/dust events … why is fractional Fe solubility highest during the dust event?

Comment: Further details have been added to this section. The sentence concerning dust estimates has been deleted. We have left the section on fractional Fe solubility where it is and refer to these values in the discussion sections of dust and biomass burning events. We discuss factors that can enhance the Fe solubility in biomass burning derived particles in section 4.6 (particle size, atmospheric processing, hydrophobic black carbon, modification with acidic species, aerosol aging). The factors that regulate fractional Fe solubility in these samples may also regulate the solubility of Al and Ti and this is discussed on page 16, lines 11-16.

P12L11 This paragraph is vague as written. "Lower enrichment factors"—lower than what? In addition, I wonder if the EF data should be presented in the results section. There is a lot of information presented here (e.g. detailed discussion of Pb, V, Mn sources) and in my opinion, it dilutes the overall message of the paper.

Comment: The section on EF has be focussed on Fe and peripheral elements (Pb,V, Mn) have been removed. Please see response to reviewer's 2 comment on this topic.

Section 4.5.1 Why is the fractional Fe solubility so high during the dust event? This is discussed in Section 4.6 to some extent, but perhaps that discussion should be moved here?

Comment: Factors that influence fractional Fe solubility are discussed in Section 4.6 and we refer the reader to that section (on page 12, line 12).

Section 4.5.2 Again, I don't disagree with anything presented here, but I do think that discussion of Cr/Mo/As is distracting—more time is spent discussing sources of these elements than in discussing the fractional solubility of Fe in this air mass, which seems skewed.

Comment: We have focused the manuscript around fractional Fe solubility, and removed much of the discussion around anthropogenic elements (Cr Mo and As) as they have little influence on fractional Fe solubility throughout the campaign. Please refer to our response to the comment made by reviewer 2 on this topic.

Section 4.5.3 The second paragraph discusses relationships between fractional Fe solubility and various biomass burning tracers, and states that fractional Fe solubility was low during fire events FG and HI (local), but higher during fire event E (distant). However, the fractional Fe solubility in the days prior to fire events FG and HI was also low—the fire plume doesn't appear to be the only source of low-solubility Fe. More generally, to me, it doesn't appear from the data in Figure 6 that the fractional Fe solubility during fire events is significantly different from that on the surrounding days. An explanation of this would be useful, I think.

Comment: Yes, the fractional Fe solubility is fairly constant ~3 % during the 21-27 June (page 13, line 9). During this time the filters were caked in soot and oxalate, levoglucosan and nss-K concentrations were high. Although we have marked on the figures the most intense fire events as determined from CO data, biomass burning occurs constantly throughout this region at this time. The campaign was heavily influenced by thousands of wild and prescribed bushfires (Milic et al., 2016). In the second paragraph, we focus on the period of low fractional Fe solubility (21-27 June) rather than fire events "FG" and "HI." This is explained on page 13, line 10.

Section 4.6 The first paragraph of this section is more suited for the introduction. In P14L17, can the conclusions for GP22 be extrapolated to the rest of the campaign, when biomass burning aerosol concentrations were low and the aerosol population was primarily dust-influenced? In P15L1, again, it seems to me that the fractional Fe solubility was generally lower over the last week of the campaign, rather than that "the fractional Fe solubility was lower when fresh EC was high". Perhaps this discussion would be better framed along the lines of "Despite the influx of aerosol from proximal fires, the fractional Fe solubility remained low"? In P16L13–14, you state an "inverse relationship between elemental carbon and soluble Fe", yet in P13L25, you state that there is no relationship between these measurements. This is directly contradictory.

Comment: The first paragraph has been moved to the introduction.

A discussion of fine particles observed in sample GP22 has been expanded on page 14, line 17-19. The sample GP22 occurred at the time of high biomass burning aerosols, and thus this sample is more indicative of particles during low fractional Fe solubility.

We have replaced the opening sentence on page 15, line 1 with that suggested by the reviewer.

On page 15, line 32, we have deleted "inverse relationship."

Conclusions

Generally, I think that the conclusions are somewhat overstated and not particularly well supported by the data, e.g.:

- P16L21 states that the fractional Fe solubility decreased to 3% during the biomass burning event, whereas the data shows that the solubility was also low prior to the event.

Comment: "event" replaced with "period."

- The discussion of the influence of oxalate on fractional Fe solubility would make sense in the introduction, but I don't think that this data set as presented supports this conclusion (are the oxalate concentrations high enough to support this conclusion? P15L26, etc., don't argue this convincingly).

Comment: Oxalate modulation has been shown to enhance fractional Fe solubility in other studies (Ito, 2015;Ito and Shi, 2016;Shi et al., 2011). We include this mechanism in our discussion as a factor that can influence mixed dust and biomass burning aerosol during transport. We do not see this enhancement in our data set as the aerosols are fresh but suggest it should be investigated in smoke plumes downwind of biomass burning sources.

- P16L28 is, in my mind, overstated—the fractional Fe solubility in fire event E is not substantially elevated over background conditions (e.g. the first sample in Figure 6).

Comment: This sentence refers to processes that could occur during transport and aging. It does not apply to what we are observing at the source.

Manuscript clarity

I often found the manuscript difficult to follow. I provide examples here, primarily from the introduction, but suggest that the manuscript be carefully edited/reorganized to maximize flow/clarity/organization on both the paragraph- and section-level scales.

Comment: The abstract and discussion has been edited and reorganised, along with sections in the methods and results.

- The first paragraph of the introduction states first that iron availability limits nitrogen fixation in nutrient-poor tropical waters (P2L12) and later that nitrogen fixation is iron limited in 75% of the world oceans (P2L22)—these thoughts could be combined.

Comment: These thoughts have been combined.

- The second paragraph of the introduction presents examples of aerosol-induced toxic algal blooms as if it were a new topic, with no link made to P2L11.

Comment: We have added a linking sentence on page 2, lines 14-16.

"Dissolved Fe can also be supplied to the surface ocean by vertical mixing, hydrothermal inputs and resuspension of marine sediments, in addition to wet and dry deposition from atmospheric sources (e.g. Tagliabue et al., 2010; Elrod et al., 2004; Mills et al., 2004)."

- The third paragraph of the introduction discusses two Australian aeolian dust paths, but in insufficient detail to picture them—what do “northwest” and “southeast” mean, exactly?

Comment: These dust paths travel northwest and southeast of the Australian continent into the adjacent waters. We have reworded the “northwest dust path” to the “transport of dust northwest of Australia.”

- The paragraph on black carbon terminology seems misplaced (P3L21–29) — perhaps this can be included in the methods section?

Comment: The terminology of black carbon has been moved to Section 2.7 in the methods.

- The sentence beginning on the last line of P3 is unclear as written.

Comment: The sentence has been rewritten on page 4, line 11-12:

“During the sampling campaign, the strongest winds were predominantly from the southeast (Fig. 1).”

- In P4L3, what is meant by “smoke”? This seems vague.

Comment: “smoke” has been replaced with “biomass burning aerosols.”

- The final paragraph of the introduction is unconvincing to me (as written—I don’t mean to imply that the study isn’t worthwhile!) … as written, it seems as though a goal is to better understand dust inputs to the Southern Ocean, whereas the rest of the introduction (and the abstract) has focused on the tropical waters north of Australia

Comment: We have removed reference to the study in Antarctica and focussed on tropical waters north of Australia rather than the Southern Ocean.

- Table 1 could perhaps be moved to the supplemental information (or, just the most important information from it could be included in Table 2)

Comment: Table 1 has been moved to Table S1 in the Supplement.

- Tenses are sometimes inconsistent (e.g. Section 2.4 has both present and past tense).

Comment: The manuscript has been checked for consistent tense.

- References to personal communications in Section 3.2 should be removed.

Comment: All references to personal communication of co-authors have been removed.

- A number of typos throughout, e.g. “particulate patter” (P8L17), “biomass burring” (P13L24)

Comment: Typos have been corrected.

- The use of A/B for dust events and A/B/C/D for trajectory types is very confusing, and requires a lot of flipping back and forth between text and figures.

Comment: 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.

- In P11L13, “contamination” doesn’t seem an appropriate word.

Comment: The sentence has been rewritten:

“The EFs of Gunn Point filters are used to aid our interpretation of mineral dust versus other aerosol sources.”

References

Aguilar-Islas, A. M., Wu, J., Rember, R., Johansen, A. M., and Shank, L. M.: Dissolution of aerosol-derived iron in seawater: Leach solution chemistry, aerosol type, and colloidal iron fraction, Marine Chemistry, 120, 25-33, 2010.

Baker, A. R., Jickells, T. D., Witt, M., and Linge, K. L.: Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean, Marine Chemistry, 98, 43-58, 2006.

Buck, C. S., Landing, W. M., Resing, J. A., and Lebon, G. T.: Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise, Geochem. Geophys. Geosyst., 7, Q04M07, 10.1029/2005gc000977, 2006.

Chen, Y., and Siefert, R. L.: Seasonal and spatial distributions and dry deposition fluxes of atmospheric total and labile iron over the tropical and subtropical North Atlantic Ocean, J. Geophys. Res., 109, D09305, 10.1029/2003jd003958, 2004.

Fishwick, M. P., Sedwick, P. N., Lohan, M. C., Worsfold, P. J., Buck, K. N., Church, T. M., and Ussher, S. J.: The impact of changing surface ocean conditions on the dissolution of aerosol iron, Global Biogeochemical Cycles, 2014GB004921, 10.1002/2014GB004921, 2014.

Ito, A.: Atmospheric Processing of Combustion Aerosols as a Source of Bioavailable Iron, Environmental Science & Technology Letters, 2, 70-75, 10.1021/acs.estlett.5b00007, 2015.

Ito, A., and Shi, Z.: Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean, Atmospheric Chemistry and Physics, 16, 85-99, 2016.

Keene, W. C., Pszenny, A. A., Galloway, J. N., and Hawley, M. E.: Sea-salt corrections and interpretation of constituent ratios in marine precipitation, Journal of Geophysical Research: Atmospheres, 91, 6647-6658, 1986.

Milic, A., Mallet, M. D., Cravigan, L. T., Alroe, J., Ristovski, Z. D., Selleck, P., Lawson, S. J., Ward, J., Desservettaz, M. J., Paton-Walsh, C., Williams, L. R., Keywood, M. D., and Miljevic, B.: Aging of aerosols emitted from biomass burning in northern Australia, Atmos. Chem. Phys. Discuss., 2016, 1-24, 10.5194/acp-2016-730, 2016.

Shi, Z., Bonneville, S., Krom, M. D., Carslaw, K. S., Jickells, T. D., Baker, A. R., and Benning, L. G.: Iron dissolution kinetics of mineral dust at low pH during simulated atmospheric processing, Atmos. Chem. Phys., 11, 995-1007, 10.5194/acp-11-995-2011, 2011.

Spolaor, A., Vallelonga, P., Gabrieli, J., Cozzi, G., Boutron, C., and Barbante, C.: Determination of Fe2+ and Fe3+ species by FIA-CRC-ICP-MS in Antarctic ice samples, Journal of Analytical Atomic Spectrometry, 27, 310-317, 2012.

Winton, H., Bowie, A., Keywood, M., van der Merwe, P., and Edwards, R.: Suitability of high-volume aerosol samplers for ultra-trace aerosol iron measurements in pristine air masses: blanks, recoveries and bugs, Atmos. Meas. Tech. Discuss., 2016, 1-32, 10.5194/amt-2016-12, 2016.

Winton, V. H. L., Bowie, A. R., Edwards, R., Keywood, M., Townsend, A. T., van der Merwe, P., and Bollhöfer, A.: Fractional iron solubility of atmospheric iron inputs to the Southern Ocean, Marine Chemistry, 177, Part 1, 20-32, http://dx.doi.org/10.1016/j.marchem.2015.06.006, 2015.

Wu, J., Rember, R., and Cahill, C.: Dissolution of aerosol iron in the surface waters of the North Pacific and North Atlantic oceans as determined by a semicontinuous flow-through reactor method, Global Biogeochem. Cycles, 21, GB4010, 10.1029/2006gb002851, 2007.