Manuscript: ACP-2016-419

Author response to referee #1

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 #1 interactive comment

The manuscript reports results from analyzing gaseous and particulate matter collected from a field campaign in Australia during the dry season. The objective is to correlate the fraction of soluble iron to markers from natural and anthropogenic sources of aerosols, and to compare the amount of soluble iron in aerosols from this site to other sites reported in the literature. Overall the manuscript is organized and describes the trends in the figures and tables in detail. The major weakness of the manuscript is that there are key observations mentioned in the manuscript from data presented in a manuscript in preparation by Mallet et al. (See pages 4, 8, 12, 13, and 14). Hence, either the authors show the relevant data from that manuscript to support their arguments or wait on submitting this manuscript till the one by Mallet et al. is published.

Comment: Snice the original submission of this manuscript, Mallet et al. has been submitted to ACP Discussions (acp-2016-731). Several companion papers from the Savannah Fires in the Early Dry Season (SAFIRED) 2014 campaign in northern Australia have also been submitted or published in ACP Discussions, including a study of biomass burning aerosol aging (Milic et al., 2016) and savannah fire emission factors (acp-2016-708).

M. Desservettaz, C. Paton-Walsh, D. W. T. Griffith, G. Kettlewell, M. D. Keywood, M. V. Vanderschoot, J. Ward, M. D. Mallet, A. Milic, B. Milievic, Z. D. Ristovski, D. Howard, G. C. Edwards, and B. Atkinson. Emission factors of trace gases and particles in tropical northern Australia. MS No.: acp-2016-708.

M. Mallet, M. Desservettaz, B. Miljevic, A. Milic, Z. Ristovski, J. Alroe, L. Cravigan, R. Jayaratne, C. Paton-Walsh, D. Griffith, S. Wilson, G. Kettlewell, M. van der Schoot, P. Selleck, F. Reisen, S. Lawson, J. Ward, J. Harnwell, M. Cheng, R. Gillett, S. Molloy, D. Howard, P. Nelson, A. Morrison, G. Edwards, A. Williams, S. Chambers, S. Werczynski, L. Williams, H. Winton, B. Atkinson, X. Wang, and M. Keywood. An overview of the Savannah Fires in the Early Dry Season (SAFIRED) 2014 campaign in northern Australia. MS No.: acp-2016-731.

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.

The comments below are minor and intended to improve the readability of the manuscript:

- The abstract is too long and contains a reference, which is not recommended. Revise for brevity and to highlight the main findings of the manuscript

Comment: The abstract has been shortened to highlight the main findings and the reference removed.

- Show correlation plots for soluble iron concentration versus oxalate and versus black carbon to support the discussion section

Comment: A correlation plot for fractional Fe solubility versus elemental carbon can be found in panel a) of Fig. S1. We have added panel b) to Fig. S1 of fractional Fe solubility versus oxalate.

- On page 3, combine paragraphs 2 and 3

Comment: Paragraphs 2 and 3 have been combined.

- On page 7, line 15, list the major cations and anions

Comment: As this paper uses oxalate and levoglucosan measurements. The heading has been changed to "2.6. Oxalate and levoglucosan"

- Revise the manuscript for long sentences (more than 3 lines in length) and shorten them

Comment: Long sentences have been edited throughout the manuscript.

- On page 9, switch the order of sentences between lines 5 and 10 to present data in Fig. 3 then Fig. 5

Comment: Sentences have been rearranged so that the references to figures are in chronological order.

- Revise the manuscript for consistency in citing figures as 'Figure' or 'Fig.'

Comment: We have followed the ACP guidelines for authors regarding the abbreviation of figures, i.e., "Fig." is used when it appears in running text and "Figure" is used at the beginning of a sentence.

- On page 10, comparisons with previous related work is summarized. It would be better to make a graph that highlights the similarities among different sites

Comment: Our fractional Fe solubility and total aerosol Fe data are compared to other Southern Hemispheric aerosol iron studies in Fig. 7. Different regions are colour coded to make visual comparison clearer.

- On page 15, cite a recent review article published on the surface and bulk chemistry of iron that is related to the discussion in this section: "Al-Abadleh, H. A., A Review on the Bulk and Surface Chemistry of Iron in Atmospherically-relevant Systems Containing Humic Like Substances. RSC Adv. 2015, 5, 45785 - 45811.",

Comment: This article has been cited on page 15 lines, 13-15. Thank you for this suggestion.

"In a review of Fe chemistry in systems containing humic-like substances, Al-Abadleh (2015) highlights the complexation and dissolution processes in which aerosol Fe solubility is enhanced with organic compounds."

- Use different types of marker shapes for Figure 7

Comment: Different shapes have been applied to the data points in Fig. 7.

- Rearrange figures in Figure S1 to enlarge font size in numbers and axis labels

Comment: The font has been enlarged in Fig. S1.

- Use different line styles for Figure S2

Comment: Different line styles have been applied to Fig. S2.

References

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.

Manuscript: ACP-2016-419

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 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?

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* $\mu g\ m^{-3}$ *with a MDL of 0.0002. Levoglucosan has no detectable blank with a MDL of 0.00002* $\mu g\ m^{-3}$*. 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 (HNO3 and HF) used in the digestion on page 5, line 30.

References

Akagi, S., Yokelson, R. J., Wiedinmyer, C., Alvarado, M., Reid, J., Karl, T., Crounse, J., and Wennberg, P.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmospheric Chemistry and Physics, 11, 4039-4072, 2011.

Andersen, A. N., Cook, G. D., Corbett, L. K., Douglas, M. M., Eager, R. W., RUSSELL-SMITH, J., Setterfield, S. A., Williams, R. J., and Woinarski, J. C.: Fire frequency and biodiversity conservation in Australian tropical savannas: implications from the Kapalga fire experiment, Austral Ecology, 30, 155-167, 2005.

Arimoto, R., Duce, R. A., and Ray, B. J.: Concentrations, sources and air-sea exchange of trace elements in the atmosphere over the Pacific Ocean, Chemical Oceanography, 10, 107-149, 1989.

Baker, A., Kelly, S., Biswas, K., Witt, M., and Jickells, T.: Atmospheric deposition of nutrients to the Atlantic Ocean, Geophysical Research Letters, 30, 2003.

Duce, R., Arimoto, R., Ray, B., Unni, C., and Harder, P.: Atmospheric trace elements at Enewetak Atoll: 1. Concentrations, sources, and temporal variability, Journal of Geophysical Research: Oceans, 88, 5321-5342, 1983.

Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., Buat-Menard, P., Hicks, B. B., Miller, J. M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L., Jickells, T. D., Knap, A. H., Reinhardt, K. H., Schneider, B., Soudine, A., Tokos, J. J., Tsunogai, S., Wollast, R., and Zhou, M.: The atmospheric input of trace species to the world ocean, Global Biogeochem. Cycles, 5, 193-259, 10.1029/91gb01778, 1991.

Gaudichet, A., Echalar, F., Chatenet, B., Quisefit, J., Malingre, G., Cachier, H., Buat-Menard, P., Artaxo, P., and Maenhaut, W.: Trace elements in tropical African savanna biomass burning aerosols, Journal of Atmospheric Chemistry, 22, 19-39, 1995.

Gelado-Caballero, M. D., López-García, P., Prieto, S., Patey, M. D., Collado, C., and Hérnández-Brito, J. J.: Long-term aerosol measurements in Gran Canaria, Canary Islands: Particle concentration, sources and elemental composition, Journal of Geophysical Research: Atmospheres, 117, 2012.

Paris, R., Desboeufs, K., Formenti, P., Nava, S., and Chou, C.: Chemical characterisation of iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX: implication for iron solubility, Atmospheric Chemistry and Physics, 10, 4273-4282, 2010.

Reimann, C., and Caritat, P. d.: Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry, Environmental Science & Technology, 34, 5084-5091, 2000.

Srinivas, B., Sarin, M., and Kumar, A.: Impact of anthropogenic sources on aerosol iron solubility over the Bay of Bengal and the Arabian Sea, Biogeochemistry, 110, 257-268, 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.

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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.

Dry season aerosol iron solubility in tropical northern Australia

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Abstract. Marine nitrogen fixation is co-limited by the supply of iron (Fe) and phosphorus in large ~~areas~~ regions of the global ocean. ~~Up to 75 % of marine nitrogen fixation may be limited by iron supply due to the relatively high iron requirements of planktonic diazotrophs.~~ The deposition of soluble aerosol ~~iron~~Fe can initiate nitrogen fixation and trigger toxic algal blooms in nitrate-poor tropical waters. ~~There is a large variability in estimates of soluble iron, related to the mixing of aerosol iron sources. Most studies assume that mineral dust represents the primary source of soluble iron in the atmosphere.~~ We present dry season soluble Fe data from the Savannah Fires in the Early Dry Season (SAFIRED) campaign in Northern Australia that reflects coincident dust and biomass burning sources of soluble aerosol Fe. ~~However, seasonal biomass burning in tropical regions is a potential source of aerosol iron that could explain the large variability of soluble iron in those regions. To investigate aerosol iron sources to the adjacent tropical waters of Australia, the fractional solubility of aerosol iron was determined during the Savannah Fires in the Early Dry Season (SAFIRED) campaign at Gunn Point, Northern Territory, Australia during the dry season in 2014. The source of particulate matter less than 10 µm (PM10) aerosol iron was a mixture of mineral dust, fresh biomass burning aerosol, sea spray and anthropogenic pollution.~~ The mean soluble and total aerosol ~~iron~~Fe concentrations were 40 and 500 ng m^{-3} respectively. ~~Fractional Fe solubility was relativity high for the majority of the campaign and averaged 8 % but dropped to 3 % during the largest and most proximal fire event.~~ Our results show that while biomass burning species may not be a direct source of soluble Fe, biomass burning may substantially enhance the solubility of mineral dust. We observed fractional Fe solubility up to 12 % in mixed aerosols. Thus, Fe in dust may be more soluble in the tropics compared to higher latitudes due to higher concentrations of biomass burning derived reactive organic species in the atmosphere. In addition, biomass burning derived particles can act as a surface for aerosol Fe to bind during atmospheric transport and subsequently be released to the ocean upon deposition. ~~Fractional Fe solubility and proxies for biomass burning (elemental carbon, levoglucosan, oxalate and carbon monoxide) were unrelated throughout the campaign. An explanation of the lack of correlation between fractional Fe solubility and elemental carbon at the biomass burning source is due to the~~

~~physical properties of elemental carbon, i.e., fresh elemental carbon aerosols are initially hydrophobic, however they can disperse in water after aging and coating with water soluble species in the atmosphere. Combustion aerosols are thought to have a high factional Fe solubility, which can increase during atmospheric transport from the source. Although, biomass burning derived particles may not be a direct source of soluble iron, they can act indirectly as a surface for aerosols iron to bind during atmospheric transport and subsequently be released to the ocean upon deposition. In addition, biomass burning derived aerosols can indirectly impact the fractional solubility of mineral dust. Fractional Fe solubility was highest during dust events at Gunn Point, and could have been enhanced by mixing with biomass burning derived aerosols. Iron in dust may be more soluble in the tropics compared to higher latitudes due to the presence higher concentrations of biomass burring derived reactive organic species in the atmosphere, such as oxalate, and their potential to enhance the fractional Fe solubility of mineral dust.~~ As the aerosol loading is dominated by biomass burning emissions over the tropical waters in the dry season, additions of biomass burning derived soluble ~~iron~~Fe could have harmful consequences for initiating nitrogen fixing toxic algal blooms. Future research is required to quantify biomass burning derived particle sources of soluble ~~iron~~Fe over tropical waters.

Key words

Iron, dust, biomass burning, soluble iron, aerosol, Australia

1 Introduction

The deposition and dissolution of aerosols containing trace metals, such as iron (Fe), into the ocean may provide important micronutrients required for marine primary production in waters where they are depleted, such as the Southern Ocean (e.g. Boyd et al., 2000). Conversely, the deposition of soluble ~~iron~~Fe can trigger toxic algal blooms in nutrient-poor tropical waters (LaRoche and Breitbarth, 2005).~~ Nitrogen fixation *Trichodesmium* is Fe-limited in around 75 % of the world oceans., assuming present aerosol Fe fluxes and sea surface temperatures (Berman-Frank et al., 2001).~~ In these waters, ~~iron~~Fe availability is a primary factor limiting nitrogen fixation (Rueter, 1988;Rueter et al., 1992;Falkowski, 1997;Knapp et al., 2016;Garcia et al., 2015).~~,~~ T~~and t~~he addition of bioavailable ~~iron~~Fe can influence inputs of newly fixed nitrogen into surface waters (Paerl et al., 1987;Rueter, 1988). A large fraction of nitrogen fixation is attributed to the filamentous, nonheterocystous cyanobacteria *Trichodesmium* (Paerl et al., 1994;Berman-Frank et al., 2001). Nitrogen fixation by *Trichodesmium* is Fe-limited in around 75 % of the world oceans (Berman-Frank et al., 2001). Nitrogen fixation has a higher ~~iron~~Fe requirement, reflected by higher Fe:C quotas of *Trichodesmium* that range between 180–214 µmol Fe mol^{-1} C (Berman-Frank et al., 2001)~~[*Berman-Frank et al., 2001*]~~, compared with other marine phytoplankton, such as diatoms, which have Fe:C quotas ranging between 1 and 7 µmol mol^{-1} (Kustka et al., 2003;Johnson et al., 1997;Rueter et al., 1992). Previous studies have investigated ~~iron~~Fe availability as a limiting factor of marine primary production surrounding ~~to the oceans surrounding~~ Australia. High ~~iron~~Fe quotas and high nitrogen fixation rates of *Trichodesmium* were observed during bloom conditions from coastal waters north of Australia (Berman-Frank et al., 2001). ~~Berman-Frank et al. (2001) calculated the potential of nitrogen fixation by *Trichodesmium* in the global ocean, and suggested that nitrogen fixation is iron-limited in around 75 % of the world oceans, assuming present aerosol iron fluxes and sea surface temperatures.~~ In the oligotrophic waters of the north Tasman Sea, southwest Pacific, a 10-fold increase in nitrogen fixation was observed ~~in response to~~after a cyclone. This ~~which~~ stimulated diazotrophy by enhanced phosphate availability in the absence of nitrate, and increased the dissolved ~~iron~~Fe supply by wet deposition of Australian dust (Law et al., 2011). 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 of atmospheric sources (e.g. Tagliabue et al., 2010;Elrod et al., 2004;Mills et al., 2004).

Aerosols are an important source of new ~~iron~~Fe to the global ocean (Boyd and Ellwood, 2010;Rubin et al., 2011). In tropical waters, several studies have shown that large toxic algal blooms, such as dinoflagellate Gymnodinium and cyanobacteria, have been stimulated by ~~an~~ atmospheric deposition of nutrients. For example, the deposition of volcanic ash and Saharan dust may have alleviated the ~~iron~~Fe limitation of toxic diazotrophic cyanophytes, thus fuelling nitrogen fixation of red tides in the eastern Gulf of Mexico (Lenes et al., 2008;Walsh and Steidinger, 2001). In addition to mineral dust, biomass burning could be a source of bioavailable ~~iron~~Fe ~~supply~~ (Guieu et al., 2005;Ito, 2015, 2013) fuelling toxic algal blooms in tropical waters. The mortality of a coral reef in 1997 in western Sumatra, Indonesia was linked to ~~iron~~Fe-fertilisation by Indonesian wildfires causing a giant red tide of *Trichodesmium* (Abram et al., 2003).

Australia is the primary source of atmospheric dust in the Southern Hemisphere, episodically supplying dust to the Tasman Sea and Southern Ocean (McTainsh et al., 2005). There are two general dust pathways from the Australian continent to the ocean (Bowler, 1976;Sprigg, 1982). First, the transport of dust southeast ~~aeolian dust~~ of Australia ~~path~~ is associated with easterly-moving frontal systems within the zonal westerly winds, and its deposition has been observed in marine sediment in the southwest Pacific Ocean and glaciers in New Zealand (Hesse and McTainsh, 2003;Johnston, 2001;Hesse, 1994;Marx et al., 2005). Second, the transport of dust ~~from the~~ northwest ~~aeolian dust~~of Australia ~~path~~ is associated with the easterly trade winds. In spite of the ubiquity of aeolian dust in Australia and the surrounding oceans, there are few studies investigating the composition of the dust on a continental scale. Some, but not all, Australian dust storms are thought to stimulate phytoplankton blooms (Shaw et al., 2008;Cropp et al., 2013;Gabric et al., 2010;Mackie et al., 2008). Soluble ~~iron~~Fe deposition models indicate that dust and combustion aerosols from the Australian continent can be deposited in other coastal regions of Australia, such as the Indian Ocean and waters north of Australia (Ito, 2015;Mahowald et al., 2005). Studies from ice cores show that Australian dust and refractory black carbon (rBC), a proxy for biomass burning, can be transported long-range to Antarctica (Revel-Rolland et al., 2006;De Deckker et al., 2010;Bisiaux et al., 2012).

~~We note that the difference in the terminology of black carbon versus elemental carbon in the literature reflects the characteristics of carbonaceous matter and the analytical method employed (Andreae and Gelencsér, 2006;Petzold et al., 2013;Bond et al., 2013). The terminology used here follows that recommended by Petzold et al. (2013), that is, the term "black carbon" is used qualitatively when referring to material that shares some of the characteristics of black carbon (carbonaceous composition combined with light-absorbing properties); "elemental carbon" refers to data derived from methods that are specific to the carbon content of carbonaceous matter using thermal desorption methods; "refractory black carbon" (rBC) is used instead of black carbon for measurements derived from incandescence methods; while mixed particles containing black carbon are referred to as "black carbon-containing particles." The data reported in this study was analysed using thermal desorption methods and is referred to as elemental carbon.~~

The fractional solubility of aerosol ~~iron~~Fe is an important variable determining ~~iron~~Fe availability for biological uptake. On a global scale, the large variability in the observed fractional ~~iron~~Fe solubility results, in part, from a mixture of ~~different~~ aerosol sources. ~~To date~~ M~~m~~ost studies ~~have~~ assume~~d~~ that mineral dust aerosols represent the primary source of soluble ~~iron~~Fe in the atmosphere (e.g. Baker and Croot, 2010). Mineral dust has a low fractional ~~iron~~Fe solubility (~0.5-2 %), whereas the presence of other soluble ~~iron~~Fe sources, such as those originating from biomass burning and oil combustion have a higher fractional ~~iron~~Fe solubility (Chuang et al., 2005;Guieu et al., 2005;Sedwick et al., 2007;Schroth et al., 2009;Ito, 2011). Although~~,~~ the total ~~iron~~Fe content of fresh biomass burning aerosols~~smoke~~ is small, around 0.01 to ~~-~~1.2 % (Maenhaut et al., 2002;Yamasoe et al., 2000;Reid et al., 2005), estimates of fractional ~~iron~~Fe solubility from fire combustion are large and variable (1 to 60 %). This large variability may be related to characteristics of the biomass, and fire as well as that of the underlying terrain (Ito, 2011;Paris et al., 2010). Ito (2015) shows that biomass burning derived soluble Fe contributes substantial inputs of soluble Fe to tropical and Southern Ocean waters downwind of Australia. Biomass burning could be an important source of soluble Fe to both tropical and Southern Ocean waters surrounding Australia.

~~An investigation of rBC deposition to the Ross Sea, Antarctica found that variability in annual deposition parallels austral dry season rBC emissions, dust and soluble iron deposition (Winton et al. (2016b). Iron associated with biomass burning may be an important source of iron to the Southern Ocean.~~ Austral dry season rBC~~C~~ emissions in the Southern Hemisphere primarily occur in the intertropical convergence zone (ITCZ) of Africa, Australia and South America (Giglio et al., 2013). ~~Australia is the closest of these regions to the Ross Sea. Here~~In Australia, biomass burning constitutes a large source of ~~annual~~ dry season aerosol emissions over northern and central Australia, and episodic austral summer wild fire in southern and eastern Australia (e.g. Meyer et al., 2008). In northern Australia, the dry season occurs from May/June (early dry season) to October-November (late dry season) (Andersen et al., 2005). To date, data for Australian ~~aerosol~~ soluble aerosol ~~iron~~Fe sources is sparse (e.g. Mackie et al., 2008;Mackie et al., 2005), and no soluble aerosol ~~iron~~Fe data exists for Australian fire sources. The dry season tropical savannah burning region in northern Australian provides an ideal location to ~~further ~~investigate biomass burning derived fractional ~~iron~~Fe solubility at the source. This study reports fractional ~~iron~~Fe solubility~~ as~~ estimates of mixed dust and fresh biomass burning (black carbon-containing particles) derived ~~iron~~Fe input to north Australian waters.~~,~~ The study was conducted as part of the Savannah Fires in the Early Dry Season (SAFIRED) campaign from the Australian Tropical Atmospheric Research Station (ATARS), Gunn Point, Northern Territory, Australia.

2. Methods

2.1. Study site

The CSIRO Oceans and Atmosphere and the Australian Bureau of Meteorology has established a station at the ATARS, Gunn Point, Northern Territory, Australia (12°14'56.6"S, 131°02'40.8"E) (Fig. 1) monitoring meteorological parameters since 2010. The SAFIRED campaign occurred at the ATARS throughout June 2014 to investigate the chemical and physical properties of aerosols and gases associated in fresh and aged smoke plumes from biomass burning. A range of atmospheric species including greenhouse gases, aerosols, and additional meteorological parameters were monitored throughout the campaign. An overview of the campaign and description of the Gunn Point study site can be found in Mallet et al. (~~[~~submitted acp-2016-731~~in prep~~)~~]~~. The Northern Territory of Australia experiences hot, humid and wet conditions during the summer months of December through to March, and dry conditions for the rest of the year. The savannah region gives rise to frequent fires between June and November. ~~Indonesia and the tropical Timor Sea lie to the north of Gunn Point. ~~The large desert regions of central Australia lie to the south. During the sampling campaign, the strongest~~strong ~~ winds were predominantly from the southeast~~ brought continental atmospheric conditions to the site ~~(Fig. 1).

2.2. Sampling and blanks

Daily aerosol filters were collected using two Volumetric Flow Controlled (VFC) high-volume aerosol samplers (Ecotech) attached with particulate matter less than 10 µm (PM10) size selective inlets (Ecotech). The samplers were operated simultaneously. The first high-volume sampler was used to collect aerosols on acid cleaned cellulose Whatman 41 filter sheets (20 x 25 cm) to determine the soluble and total fraction of aerosol ~~iron~~Fe and other trace elements. ~~All sample preparation and analysis was conducted in a trace metal clean laboratory (class 100 metal-free environment with high-efficiency particulate arrestance (HEPA) filtered air) at Curtin University following the ultra-clean methodology. Details for ultra-pure reagents, ultra-pure water, acid-washing of apparatus and Whatman 41 filters and filter sub-sampling are described in Winton et al. (2016a).~~

The second sampler was used to collect aerosol samples on quartz filters for elemental carbon and major cation and anion measurements. The high-volume aerosol samplers were located on the roof of a shipping container (at a height of 5 m above ground level (agl)) at the ATARS. ~~A total of 23 trace metal aerosol filters were sampled daily between 4 and 27 June 2014 and are described in Table 1.~~

Loading and changing of aerosol collection substrates was carried out in a designated clean area at the ATARS. Aerosol laden filters were transferred into the individual zip-lock plastic bags immediately after collection and stored frozen until analysis at Curtin University and CSIRO Ocean and Atmosphere. A total of 23 trace metal aerosol filters were sampled daily between 4 and 27 June 2014 and are described in Table S1.

For the trace element work, three types of filter blanks were carried out; i) laboratory filter blanks (n=6) (acid-washed Whatman 41 filter papers that underwent the laboratory procedures without going into the field), ii) procedural filter blanks (n=4) (filters that had been treated as for normal samples, i.e., acid-washed, but which were not otherwise used. Once a week, during daily filter change over, a procedural blank filter was mounted in the aerosol collector for 10 minutes without the collector pump in operation. This type of filters provides an indication of the operational blank associated with the sampling procedure), and iii) 24-hour exposure filter blanks sampled at the beginning and end of the field campaign (n=2) (filters treated like a procedural blank, but left it in the collector for 24-hours without switching the collector on). Exposure blank filters for the elemental carbon and major ion measurements were run simultaneously with the trace element exposure blank filters.
~~All sample preparation and analysis was conducted in a trace metal clean laboratory (class 100 metal-free environment with high-efficiency particulate arrestance (HEPA) filtered air) at Curtin University following the ultra-clean methodology. Details for ultra-pure reagents, ultra-pure water, acid-washing of apparatus and Whatman 41 filters and filter sub-sampling are described in Winton et al. (2016a).~~

~~Loading and changing of aerosol collection substrates was carried out in a designated clean area at the ATARS. Aerosol laden filters were transferred into the individual pre-acid-washed zip-lock plastic bags immediately after collection and stored frozen until analysis at Curtin University. Three types of filter blanks were carried out; i) laboratory filter blanks (n=6) (acid-washed Whatman 41 filter papers that underwent the laboratory procedures without going into the field), ii) procedural filter blanks (n=4) (filters that had been treated as for normal samples i.e. acid-washed, but which were not otherwise used. Once a week, during daily filter change over, a procedural blank filter was mounted in the aerosol collector for 10 minutes without the collector pump in operation to give an indication of the operational blank associated with the sampling procedure), and iii) 24 hour exposure filter blanks sampled at the beginning and end of the field campaign (n=2) (filters treated like a procedural blank, but left it in the collector for 24 hours without switching the collector on).~~

2.3. Trace element analysis

All sample preparation and analysis for the trace element work was conducted in a trace metal clean laboratory (class 100 metal-free environment with high-efficiency particulate arrestance (HEPA) filtered air) at Curtin University following trace metal ~~metal~~clean practices (e.g. Cutter et al., 2010). Details for ultra-pure reagents, ultra-pure water, acid-washing of apparatus and Whatman 41 filters and filter sub-sampling are described in Winton et al. (2016a).

2.3.1. Water solubility of aerosol iron

There are a number of published methods for determining iron solubility, and a number of operational definitions of iron solubility. The discrepancy in soluble Fe methods, and the associated uncertainties, makes it difficult to compare results from different studies (Meskhidze et al., 2016). Although there are few estimates of soluble Fe in Australian dust and aerosols, for consistency we use the instantaneous water leaching scheme that was used in the Australian studies (Winton et al., 2016a;Winton et al., 2015). It is widely reported in the literature that soluble Fe concentrations of aerosols decrease exponentially with subsequent leaches (e.g. Wu et al., 2007;Fishwick et al., 2014;Aguilar-Islas et al., 2010). To determine how many leaches were required to extract the concentration of instantaneous soluble Fe from our samples, we tested sample GP5 with 10 passes of 50 mL ultra-pure water. The experiment was repeated three times using three separate punches from the same filter sample. The exponential decrease in the soluble Fe concentration is illustrated in Fig. S2, and shows that soluble Fe is leached from the sample even after 10 leaches. Therefore, soluble elements (Al, Ti, V, Mn, Fe, Pb) were extracted from the Gunn Point filters using an instantaneous flow-through water leach consisting of 20 separate passes of 50 mL of ultra-pure water. A total volume of 1000 mL was filtered through each aerosol filter. Leachates were collected in acid-washed polypropylene (PP) Corning® tubes and acidified to 1 % ultra-pure HCl. Soluble elements were extracted from aerosol filters (GP1-23), exposure blanks (EB1-2), and procedural blanks (PB1-4). ~~Soluble elements (Al, Ti, V, Mn, Fe, Pb) were extracted from the filter using an instantaneous flow-through water leach consisting of 20 separate passes of 50 mL of ultra-pure water. A total volume of 1000 mL was filtered through each aerosol filter.~~

~~Soluble elements were extracted from aerosol filters (GP1-23), exposure blanks (EB1-2), and procedural blanks (PB1-4). Soluble elements (Al, Ti, V, Mn, Fe, Pb) were extracted from the filter using an instantaneous flow-through water leach consisting of 20 separate passes of 50 mL of ultra-pure water. A total volume of 1000 mL was filtered through each aerosol filter. In this test, we leached sample GP5 with 10 passes of 50 mL ultra-pure water. The experiment was repeated three times using three separate punches from the same sample.~~Following the test on sample GP5, only leaches 1-4, 6, 10 and 20 were collected and analysed. The concentration of the unanalysed leachates 5, 7-8 and 11-19 was estimated by fitting a power law curve to the soluble Fe concentration in leachates 1-4, 6, 10 and 20 for each sample. ~~Only leaches 1-4, 6, 10 and 20 were collected and analysed, following a test where we determined the maximum number of leaches required to leach the majority of soluble iron from the aerosols. In this test, we leached sample GP5 with 10 passes of 50 mL ultra-pure water. The experiment was repeated three times using three separate punches from the same sample. Leachates were collected in 50 mL acid-washed polypropylene (PP) Corning® tubes and acidified to 1 % ultra-pure HCl. Leaches 5, 7-8 and 11-19 were estimated by fitting a power law curve to the each sample.~~ Total ~~water~~ soluble ~~trace elements~~Fe (and trace elements) ~~were~~ was calculated by summing the soluble ~~iron~~Fe concentration extracted from 20 leaches. The leachates from sample GP22 (as an example of sample with a particularly high soluble Fe concentration) were filtered through 0.2 μm acid-cleaned Polyvinylidene Fluoride

(PVDF) syringe filters. Blank concentrations for exposure blank and procedural blank filters averaged ~0.4 ng g^{-1} and 0.5 ng g^{-1} of soluble ~~Fe~~ Fe respectively.

~~(Winton et al., 2016a;Winton et al., 2015)~~

2.3.2. Total iron concentrations

Total PM10 trace element (Na, Al, K, Ti, V, Cr, Mn, Fe, Mo, Pb, As) concentrations were determined following recommendations from the 2008 GEOTRACES intercalibration experiment for the analysis of marine aerosols (Morton et al., 2013). Details for HNO_3 and HF acid digestion of filter samples and certified reference materials (MESS-3 marine sediment, National Research Council, Canada, and QC-TMFM-A spiked trace metals (1-10 µg of trace metal per filter) on nitrocellulose filter (TMF), High Purity Standards) can be found in Winton et al. (2016a). Recovery rates for elements are reported in Table S2~~1~~. Blank concentrations for Savillex® digestion beakers, exposure blank, procedural blank and laboratory blank filters averaged ~4 ng g^{-1} (n=3), ~150 ng g^{-1} (n=2), ~140 ng g^{-1} (n=4), and ~140 ng g^{-1} (n=6) of total ~~iron~~Fe respectively. The non-sea salt-potassium (nss-K) fraction of total K was obtained by subtracting the contribution of sea salt derived K from the measured K concentrations (nss-K = K -0.037 x 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).

2.3.3. High-resolution inductively coupled plasma mass spectrometry analysis

Leachates and resuspended total digests were analysed by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Element XR ThermoFisher) at Curtin University following Winton et al. (2016a). All samples and standards were prepared on a similar matrix basis. During the course of the sample sequence, an EPA standard (Cat. #ICP-200.7-6 Solution A, High Purity Standards) was measured regularly for quality control~~ (QC)~~. Laboratory vial blanks~~, were~~ also measured regularly during the course of the sample sequence, were determined by carrying out identical analytical procedures as the leachates but vials were filled with ultra-pure water rather than the leachate. Leachate concentrations were corrected for laboratory blanks, and the total digest concentrations corrected for the Savillex® digestion beaker blanks. Measured trace elements and the spectral resolutions, along with typical operating conditions, are reported in Table S3~~2~~.

2.4. Air mass back trajectories

To identify the source region of air masses arriving at Gunn Point, we used hourly 5-day (120-hr) back trajectories (ending at 12 m agl) to reconstruct atmospheric circulation leading up to, and during, individual events. Air mass back trajectories were produced using the 'Trajectory program' based on the NOAA ARL HYbrid Single-Particle Lagrangian Integrated Trajectory (HYsplit) model (Draxler and Rolph, 2003) (http://ready.arl.noaa.gov/HYSPLIT.php). Global Data Assimilation System model files (GDAS) obtained from NOAA ARL FTP (http://ready.arl.noaa.gov/gdas1.php) were used to drive the model. The resolution used was 0.5 degrees.

2.5. Radon concentrations

Natural radioactive noble gas radon-222 (radon) is a useful quantitative indicator of diurnal to synoptic scale mixing processes within the continental lower troposphere (Chambers et al., 2015), and a suitable tracer for continental air (e.g. Dörr et al., 1983). This is because radon has a half-life of 3.8 days and only one source and sink i.e. radon is solely produced from terrestrial surfaces and is lost from the atmosphere by radioactive decay. The ANSTO-built 700 L dual-flow-loop two-filter radon detector (e.g. Whittlestone and Zahorowski, 1998;Chambers et al., 2014) samples air from 12 m above ground level (a.g.l.). A coarse aerosol filter and dehumidifier are installed "upstream" of the detector, as well as a 400 L delay volume to ensure that thoron (^{220}Rn, half-life 55 s) concentrations in the inlet air stream are reduced to less than 0.5 % of their ambient values. The detector's response time is around 45 minutes, and its lower limit of determination is 40 - 50 mBq m^{-3}. Calibrations are performed on a monthly basis by injecting radon from a PYLON 101.15 ± 4 % kBq Ra-226 source (12.745 Bq min^{-1} ^{222}Rn), traceable to NIST standards, and instrumental background is checked every 3 months. The time series from the Gunn Point campaign has been separated into: a) advective contributions (essentially afternoon-to-afternoon interpolated values, reflecting the air mass fetch history over the last two weeks), and b) diurnal variability (the residual, indicative of change in mixing depth) following the method of Chambers et al. (2015).

~~The time series for the Gunn Point campaign duration has been separated into contributions from a) advective (reflects the air mass fetch history over the last two weeks), and b) diurnal variability (indication of the change in mixing depth) following Chambers et al. (2015). The advective and diurnal components of the radon time series were integrated to daily values based on a noon-to-noon integration window.~~

2.6. Oxalate and levoglucosan~~Major cation and anion~~

~~Major cation and anion measurements, including~~ O~~o~~xalate and levoglucosan measurements~~,~~ were performed on the PM10 quartz filters at CSIRO Ocean and Atmosphere. The filters were Pall tissuquartz filters p/n 7204, baked~~ them~~ at ~~40~~ 600 °C for 4-8 hours before use and stored frozen after sampling until analysis. A 6.25 cm^2 section was cut out of the filter and extracted in 5 mL of ultra-pure water. The quartz filter extracts were analysed for major water soluble ions by suppressed ion chromatography (IC) and for anhydrous sugars including levoglucosan by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Iinuma et al., 2009;Hibberd et al., 2013). Three exposure blanks were analysed alongside the sample filters. The oxalate blank, calculated using an average collection volume of 1575 m^3, was 0.0009 µg m^{-3} with a MDL of 0.0002.~~,~~ W~~w~~hile levoglucosan had~~s~~ no detectable blank with a MDL of 0.00002 µg m^{-3}. All sample concentrations were blank corrected.

2.7. Elemental carbon

Elemental carbon analysis was performed on the PM10 quartz filters at CSIRO Ocean and Atmosphere using a DRI Model 2001A Thermal-Optical Carbon Analyser following the IMPROVE-A temperature protocol (Chow et al., 2007). We note that the difference in the terminology of black carbon versus elemental carbon in the literature reflects the characteristics of carbonaceous matter and the analytical method employed (Andreae and Gelencsér, 2006;Petzold et al., 2013;Bond et al., 2013). The terminology used here follows that recommended by Petzold et al. (2013), i.e~~that is~~, the term “black carbon” is used qualitatively when referring to material that shares some of the characteristics of black carbon (carbonaceous composition combined with light-absorbing properties); “elemental carbon” refers to data derived from methods that are specific to the carbon content of carbonaceous matter using thermal desorption methods; “refractory black carbon” (rBC) is used instead of black carbon for measurements derived from incandescence methods; while mixed particles containing black carbon are referred to as “black carbon-containing particles.” The data reported in this study was analysed using thermal desorption methods and is referred to as elemental carbon.

3. Results

3.1. Air mass back trajectories

We identified predominate fetch regions that gave rise to particular events; a) ‘inland, low population density,’ b) ‘coastal, moderate urban/industrial activity,’ c) ‘major urban/industrial activity,’ and d) ‘southerly.’ ~~No trajectories fell in the ‘mainly oceanic’ category.~~ The mean trajectory for each group was calculated and these representative trajectories are indicated in Fig. 1.

3.2. Biomass burning events during the campaign

The campaign was heavily influenced by thousands of proximal wild and prescribed bushfires (Milic et al., 2016). A number of biomass burning markers were used to identify major burn events during the campaign, including carbon monoxide (CO) ~~[*Desservettaz et al.*, 2016]~~, levoglucosan ~~[*Selleck et al.*, 2016]~~, oxalate, ~~[*Selleck et al.*, 2015]~~ and elemental carbon (Milic et al., 2016; Desservettaz et al., submitted acp-2016-708; Mallet et al., submitted acp-2016-731)~~[*Selleck et al.*, 201]~~. Nine burn events were identified, with ~~the~~ three ~~major~~ intense ~~events~~ episodes occurring on the 9 June (fire event “E”), 25 June (fire event “FG”) and 26-27 June 2014 (fire event “HI”) ~~2014 ([~~Mallet et al., submitted acp-2016-731~~*Mallet et al*., in prep)]~~. Smoke transported to the ~~Gunn Point~~ATARS during~~in~~ fire event “E” comprised of~~was~~ both distally sourced fires, i.e., >2~~4~~00 km, and locally sourced fires, i.e., within 5 km (Mallet et al., submitted acp-2016-731). Fire locations were obtained from the Sentinel Hotspot system (MODIS and VIIRS satellites) (Milic et al., 2016). ~~,~~ Whereas,~~while~~ the source of emissions ~~smoke~~ f~~rom~~or the largest fire events “FG” and “HI” were~~as~~ proximal, i.e., within 10~~5~~ km of the ATARS. ~~(fire locations from Sentinel Hotspot (MODIS and VIIRS satellites); (Milic et al., 2016)*Mallet et al*. [in prep]).~~ These high intensity fire events were accompanied with smouldering burning conditions that resulted in high organic loadings and high levoglucosan concentrations. Due to the different time periods the CO data (minute) and aerosol samples (daily) integrate, we have grouped fire events “F” and “G” into one event (fire event “FG”) and “H” and “I” into another event (fire event “HI”) for this study. ~~C3 tree burning was~~

~~identified from δCO_2 during the 25 June burning event [Paton-Walsh et al., 2016].~~ In addition, concentrations of ~~non-sea salt-potassium (~~nss-K~~)~~ and nss-K normalised relative to other elemental concentration are good indicators of biomass burning (Yamasoe et al., 2000;Maenhaut et al., 2002). There is good agreement between nss-K concentrations and ~~carbon monoxide (~~CO~~)~~ (r^2=0.55) (Fig. S1). There is also a good correlation between nss-K and elemental carbon concentrations (r^2=0.74) (Fig. S1). Following Guieu et al. (2005), we normalise nss-K to Fe and compare the ratio to crustal aerosols (nss-K/Fe=0.49; Wedepohl (1995)) and polluted aerosols (nss-K/Fe=0.27; urban particulate m~~p~~atter – standard reference #1648, NIST). During the campaign the nss-K/Fe ratio ranged between 0.2-4.9. This relativity large range was similar to nss-K/Fe of 0.63-1.8 for Mediterranean summer fires in 2003 (Guieu et al., 2005), nss-K/Fe of 2.0 for biomass burning aerosols for the Arabian Sea and the Bay of Bengal (Srinivas et al., 2012), and nss-K/Fe of 0.51 for the West African Sahel biomass burning (Paris et al., 2010). These studies suggested that the higher ratio reflected a primarily fire origin for nss-K. The nss-K/Fe ratio was especially high during the three fire events in this study (nss-K/Fe ~4) and during~~ the~~ high elemental carbon concentrations between 21-27 June (nss-K/Fe~2.2), compared to non-fire events (nss-K/Fe ~1.3). Even the lowest nss-K/Fe of 1.3 during the campaign is particularly high compared to crustal aerosols. This high ratio suggests that even at times when there are no major fire events, background biomass burning can still contribute Fe to aerosols during Australian dry season.

3.3. Sequential iron leaching

To determine the number of ultra-pure water leaches required to leach the majority of water soluble Fe from the Gunn Point aerosol filters, we conducted a test on ~~the~~ sample GP.~~5~~ T~~sample where t~~hree filter aliquots were leached with 10 sequential passes of 50 mL of water. The leaching results of this test in Fig. S2 show that there is an exponential decrease in soluble Fe extracted with successive leaches. Even after 1 L of ultra-pure water was passed through the aerosol filter, soluble Fe was still being extracted. We therefore leached each sample with 20 passes of ultra-pure water totalling 1 L. We acknowledge that beyond 20 leaches, soluble Fe could continue to ~~be~~ leach~~ed~~ out of the aerosol~~ filter~~s. Thus, t~~and thus t~~he data reported here reflect "instantaneous" soluble Fe and may underestimate the total concentration of soluble Fe over greater leach volumes. Figure 2 highlights the percentage of soluble Fe in each leach. Similar to other studies of instantaneous soluble Fe, around half of the soluble Fe is extracted in the first leach. The leachates from GP22 were re-filtered through 0.2 µm membranes to calculate the <0.2 µm soluble Fe fraction of the total soluble Fe. The concentration of soluble Fe in the <0.2 µm fraction of the leachate contained 70 % of the total soluble Fe in GP22 and follows the same exponential decreases with successive leaches. Leachates showed a large variability in their colour, and visual observation after particle settling showed that they contained a large number of very fine particles even in the <0.2 µm fraction.

3.4. ~~Aerosol iron~~Trace element mass concentrations

Total and soluble PM10 trace element concentrations are illustrated in Figs. 3-5. Total PM10 aerosol Fe ranges from 60-1164 ng m^{-3}, while soluble aerosol Fe ranges from 7-141 ng m^{-3}. ~~Likewise, a~~A strong linear correlation was found between the total PM10 trace elements of Fe, Al, V and Ti, i.e., total Fe and total Al (r^2=0.96), total Fe and total Ti (r^2=0.98), and total Fe and total V (r^2=0.99) (Figs. 3 and S3). Likewise, a~~A~~ strong linear correlation between~~ in~~ the soluble trace elements of Fe, Al, and Ti was found during the campaign (Figs. 5 and Fig. S3), i.e., soluble Fe and soluble Al (r^2=0.97), and soluble Fe and soluble Ti (r^2=0.86). ~~Likewise, a strong linear correlation was found between the total PM10 trace elements of Fe, Al, V and Ti, i.e., total Fe and total Al (r^2=0.96), total Fe and total Ti (r^2=0.98), and total Fe and total V (r^2=0.99) (Fig. 3).~~ There is considerable temporal variability in ~~water~~ soluble and total trace elements throughout the campaign. Two distinct events in soluble Al, Ti, and Fe and total Al, Ti, V, and Fe are observed on the 7-8 June 2014 (~~e.g.~~ GP4-5; 78-141 ng m^{-3} of soluble Fe and 1158-1164 ng m^{-3} of total Fe), and 14-15 June 2014 (~~e.g.~~ GP11-12; 52-92 ng m^{-3} of soluble Fe and 677-928 ng m^{-3} of total Fe) (Figs. 4 and 6). On the 20 June 2014~~,~~ high concentrations of these crustal like elements (total and soluble Al, Ti, V, Fe) were also observed (~~e.g.~~ GP17; 67 ng m^{-3} of soluble Fe and 1129 ng m^{-3} of total Fe) and are associated with ~~marine~~ coastal air masses ~~conditions~~(Fig. 1; trajectory type “b”). ~~In addition,~~T~~ t~~otal Cr, As, Mo, V, and Na also peaked during ~~the marine~~ coastal conditions ~~on the 20 June~~ (Fig. 5). During the fire events “E”, “FG” and “HI” on the 9, 25 and 26-27 June, total As, Mn, Pb, and soluble V concentrations were high~~This same set of total trace elements (Cr, As, Mo, and V) also peaked on the 9 June during fire event “E”~~ (Fig. ~~5~~4). ~~During the three fire events “E”, “FG” and “HI” on the 9, 25 and 26-27 June, daily integrated CO and nss-K were high at the same time as total As, Mn, Pb, and soluble V, Mn, Pb (Fig. 4).~~

3.5. Dry deposition iron flux

Estimates of the Fe dry deposition rate (F_{dry}) to adjacent north Australian surface waters were calculated using Eq. (1), and the ~~from the~~ total and soluble Fe concentrations ($C_{aerosol}$) reported from this study. We apply ~~using~~ a dry deposition velocity (V_{dry}) of 2 cm s^{-1} for coastal areas (Duce et al., 1991)~~,~~ following Baker et al. (2003) for aerosols collected along a transect in the Atlantic Ocean and Baker et al. (2007) for the atmosphere over the tropical Atlantic Ocean. Estimates of Fe dry deposition rates for Gunn Point aerosols are reported in Table 1~~2~~.

$$F_{dry} = C_{aerosol}\ x\ V_{dry\ deposition} \tag{1}$$

4. Discussion

4.1. Iron mass concentrations

~~Total PM10 Fe concentrations during the fire events (0.06-1.2 µg m^3; Fig. 3) are in good agreement with fire aerosol studies reported from the Alta Floresta, Amazon forest, Brazil between 1996-1998, which range from 0.3 to 1.2 µg m^{-3} of total Fe (Maenhaut et al., 2002).~~ The soluble Fe concentrations at Gunn Point (7-~~ to~~ 141 ng m^3) are less than soluble Fe concentrations reported in smoke from the Mediterranean and West African Sahel (350 ng m^3; Guieu et al. (2005)) and (130 ng m^3; Paris et al. (2010)) respectively. There is sparse total and soluble aerosol Fe concentration data ~~from~~ for Australian aerosols, however our estimates (0.06-1.2 µg m^3; Fig. 3) agree with reported total Fe concentrations at Jabiru, northern Australia (148 ng m^{-3}), at Sydney, New South Wales (150 ng m^{-3}) and modelled values for the north Australia coastal area (200-1000 ng m^{-3}) (Mahowald et al., 2009; and references within). Compared to aerosol Fe from other tropical regions, our total Fe estimates ~~at the~~from Australian ~~source~~ are in good agreement with biomass burning aerosol studies reported from the Alta Floresta, Amazon Forest, Brazil between 1996-1998, which range from 0.3 to 1.2 μg m^{-3} of total Fe (Maenhaut et al., 2002). Total Fe concentrations decrease from the source to the open ocean e.g. ~~greater than~~ aerosol Fe concentrations reported for the tropical Atlantic open ocean range from ~~(total Fe~~ 6 to ~~-~~56 ng m^{-3} for total Fe and ~~soluble Fe~~ 6 to ~~-~~28 ng m^{-3} for soluble Fe~~)~~ (Baker et al., 2006).~~.~~

4.2. Dry deposition estimates of soluble and total iron

Estimates of soluble and total PM10 Fe dry deposition fluxes are reported in Table 1~~2~~ and range from 0.2 ± 0.4~~1~~ to 4 ± 9~~2~~ μmol m^{-2} d^{-1} for soluble Fe and 2 ± 4~~1~~ to 36 ± 72~~18~~ μmol m^{-2} d^{-1} for total PM10 Fe. The dry deposition Fe estimates for air over Gunn Point are compared to other aerosol studies from the Southern Hemisphere and topical regions. The mean soluble Fe dry deposition flux (~1 μmol m^{-2} d^{-1}) is greater than soluble Fe dry deposition fluxes over open ocean tropical Atlantic waters (0.01-0.1 μmol m^{-2} d^{-1}) (Baker et al., 2003). The estimates at Gunn Point are also higher than those reported for the Southern Ocean, for example, 2-7 nmol m^{-2} d^{-1} reported by Bowie et al. (2009), 0.04-3 nmol m^{-2} d^{-1} reported by Wagener et al. (2008), 2-7 nmol m^{-2} d^{-1} reported by Baker et al. (2013) for the South Atlantic, and 0.1-7 nmol m^{-2} d^{-1} for baseline air over the Southern Ocean reported by Winton et al. (2015). Estimates of total PM10 Fe dry deposition fluxes at Gunn Point are higher than those for the Southern Ocean (0.8-120 nmol m^{-2} d^{-1}) (Winton et al., 2015) and the South Atlantic (100–300 nmol m^{-2} d^{-1}) (Baker et al., 2013). The Gunn Point data are in good agreement with estimates from global models for the north Australia coastal region. Mahowald et al. (2009) estimates total Fe deposition in ~~the~~ north Australia to be 0.04-1 g m^{-2} y^{-1}, and our mean total PM10 Fe flux of 0.3 g m^{-2} y^{-1} falls within this range.

4.3. Fractional iron solubility

The fractional Fe solubility ranged from 2 % to 12 % during the study (Figs. 6 and 7). These estimates are within the 0.6 to 40 % range of fractional Fe solubility reported for biomass burning (Paris et al., 2010;Bowie et al., 2009;Ito, 2011;Ito, 2015;Guieu et al., 2005). Fractional Fe solubility was highest between 4 and 20 June with a mean fractional Fe solubility of 10 ± 2 %. After 20 June, the fractional Fe solubility dropped to 3 ± 1 % between the 21 and 27 June when fires were proximal to the ATARS. ~~These estimates are similar to dust estimates around 0.5-2 % at relatively high Fe mass concentrations.~~ These trends in fractional Fe solubility over the campaign are not unique to Fe; the variation of fractional Al and Ti solubility paralleled that of fractional Fe solubility (Fig. 6). During dust event “A” (see Section 4.5.1) fractional Fe solubility peaked at ~12 %, fractional Al solubility at ~14 %, and fractional Ti solubility at ~5 % (Fig. 6). Fractional Al and Ti solubility also decreased on 24 June from 10 ± 2 % to 3 ± 1 % for Al and from 6 ± 2 % to 2 ± 1 % for Ti (Fig. 6). On the other hand, f~~F~~ractional Mn solubility was relatively high and constant throughout the campaign and averaged ~72 ~~%~~ ± 11 %. The factors that regulate fractional Fe solubility in these samples may also regulate the solubility of Al and Ti but not Mn. ~~Fractional Mn solubility was highest during fire events “FG” and “HI” when the fractional solubility of Ti and Al was low.~~

A synthesis of global aerosol Fe solubility data sets, complied by Sholkovitz et al. (2012), displayed an inverse hyperbolic relationship between the total Fe concentration and fractional Fe solubility (Fig. 7). This characteristic relationship is common over large regions of the global ocean, and has been attributed to the mixing of mineral dust with a low Fe solubility and other soluble Fe aerosols from combustion sources (e.g. Sedwick et al., 2007). We have plotted the Gunn Point aerosol Fe data with the Southern Hemisphere compilation in Fig. 7. Our data sits within two narrow clusters i) moderate fractional Fe solubility and moderate total PM10 aerosol Fe loading between the 4 and 19 June and ii) low fractional Fe solubility and low total PM10 aerosol Fe loading between the 24 and 26 June (highlighted in Fig. 7).

4.4. Enrichment factor analysis

Crustal enrichment factors (EFs) were calculated using the Wedepohl (1995) compilation of the continent crust to determine the contribution of mineral dust to the observed total elemental concentrations. Total Ti was used as a marker for mineral dust. For an element (Z) in a sample, the EF relative to Ti is calculated using Eq. (2).

$$EF = \frac{(Z/Ti)_{sample}}{(Z/Ti)_{crust}} \qquad (2)$$

The ~~enrichment factors~~EFs of Gunn Point filters are used to aid our interpretation of mineral dust ~~evaluate the level of contamination from mineral dust~~ versus other aerosol sources. We recognise limitations of using EFs for this purpose, such as whether the reference material (Ti) is representative of mineral dust in the atmosphere compared to the crust (Reimann and Caritat, 2000;Arimoto et al., 1989). ~~From the EF reported in Table 3, two groups of trace elements were identified. The first was Al and Fe which have low EFs between 0.6–1.3 throughout the campaign.~~ The majority of EFs in Table 2 are low, i.e., EF<5. Enrichment factors in this range are similar to the upper continental crust ~~(i.e., EF between 0.7 and 2)~~, suggesting that these trace metals might have originated from that source (Duce et al., 1983;Gelado-Caballero et al., 2012). Aerosol Fe has an EF between 0.9 and 1.3 and does not show Fe enrichment~~, implying that anthropogenic pollution was not a dominant source of Fe to Gunn Point.~~. The low EFs imply that biomass burning is a relatively unimportant source of Fe in this study. However, the low values can be explained by processes, such as entrainment of fine soil particles into flames and smoke plumes, that could add Fe to the aerosol. This indirect contribution of Fe aerosol could be significant.

~~The second group of trace elements consists of Cr, Mn, and Pb, and nss-K which had maximum EFs between 5 and 12 (i.e., moderate enrichment >2 EF <10 to enriched EF >10), indicating mixed sources. Cr showed moderate enrichment (EF of ~4) during the marine event, and also on the 13 June (EF of 8) when back trajectories crossed coastal Queensland (i.e., trajectory type "B"). Anthropogenic Cr could be sourced from industry and combustion (Pacyna and Nriagu, 1988).~~

~~Manganese, Pb and nss-K were enriched at three times throughout the campaign. Mn enrichment could be associated with particles that became airborne by soil dispersion or anthropogenic emissions (e.g., smelting and unleaded car fuel) (e.g. Parekh, 1990). Atmospheric Pb originates from the geological weathering, smelting, burning of unleaded fuel, and coal combustion~~

~~(e.g. Bollhöfer et al., 1999;Bollhöfer and Rosman, 2000;Bollhöfer and Rosman, 2001). The air mass back trajectories showed that during the elevated EF of Mn, Pb and nss-K, the wind direction was from the southeast and the fetch area included major cities and industrial areas in Brisbane (i.e. trajectory types “A” and C” (Fig. 1). Manganese (EF up to 5), Pb (EF between 5 and 12) and nss-K (EF between 3 and 6) showed moderate enrichment during fire events “E”, and “FG.” Enrichment of these elements also occurred during the 16-18 June when trajectories came from the south and passed over major smelting sites i.e. Port Pire and Olympic Dam in South Australia and Mt Isa, Queensland (i.e., trajectory type “D”). The enrichment factors and air mass back trajectories suggest that both smelting and biomass burning are sources of Mn, Pb and nss-K aerosols at these three times.~~

~~Lead can also originate from resuspension of contaminated material. Enrichment factors for Pb during dust events “A” and “B” were similar to the upper crust suggesting a dust source for aerosol Pb at this time. Enrichments factors of V were constant throughout the campaign, and ranged from 1.6 to 3 indicating the moderate EF for V could be related to contamination from both atmospheric mineral dust and fuel oil burning e.g. from ship exhaust (Desboeufs et al., 2005;Jang et al., 2007;Hope, 2008).~~

~~Lower enrichment factors have been observed in marine air masses at Cape Verde (collected on a 30 m tower), indicating that the elements were likely of crustal origin. On the other hand, higher EFs have been reported in marine air masses that crossed Europe and North America, indicating that the elements were of anthropogenic origin (Fomba et al., 2012). The low EF in Al and Fe and higher EF in Mn, Cr, nss-K and Pb during fire events and air masses that passed over major smelting sites are likely to also reflect a combination of crustal, marine and anthropogenic aerosols.~~

4.5. Aerosol sources

Based on a combination of radon, air mass trajectories, enrichment factor analysis and biomass burning markers, trace elements have been grouped into three sources: dust, biomass burning and ~~marine~~ coastal sources.

4.5.1. Dust events

Dust events “A” and “B” are characterised by peaks in total PM10 Al, Ti, Fe and V, and correspond to low diurnal radon, i.e., when conditions are well mixed (Fig. 3). During these two dust events, air mass back trajectories corresponded to times when the air mass passed over central Australian desert~~ and low population areas of inland Australia~~, i.e., dust event “A”: trajectory type “c,” and dust event “~~-~~B”: trajectory type “d,” (Fig. 1). Enrichment factors of Al (EF of 0.6-0.7), V (EF of 1.8-2.0) and Fe (EF of 1.0-1.1) during these two dust events suggest that these trace metals have a similar composition to the upper crust, ~~(~~i.e., EF between 0.7 and ~~-~~2) and thus most likely originate from crustal material. Soluble concentrations of Fe, Al, Ti, Mn and V were high during dust events “A” and “B”. Fractional Fe solubility was highest in dust event “A” (12 %). Factors that influence fractional Fe solubility in mixed biomass burning and mineral dust sources are discussed in Section 4.6).

4.5.2. S~~Anthropogenic and s~~ea spray sources ~~in marine~~during coastal conditions

On the 20 June 2014 ~~marine~~ coastal conditions were identified by a decrease in aerosol particle counts and a change in the particle size distribution from unimodal to bimodal with modes at 20 nm and 70 nm (~~[~~Mallet et al., ~~in prep~~submitted acp-2016-731)~~]~~. During these conditions, total Na peaked to 3.1 μg m^{-3} and~~dd~~ the Na/Mg ratio was similar to seawater which is indicative of sea spray (Figs. 4-6). The Na signal was greater during times of low advective radon, i.e. when air masses were predominantly spending less time over land and more time over ocean regions. Total PM10 Al, Ti, Fe, and V~~, as well as total PM10 Cr, Mo and As~~ peaked during these conditions. There was a moderate rise in soluble Al, Ti and Fe. Enrichment factors for Al, V and Fe during ~~marine~~ coastal conditions show that these trace metals have a similar composition to the upper crust (i.e., EF 0.7-2) and might originate from crustal material. Fractional Fe solubility was ~6 % in the ~~marine~~ coastal air mass. During these conditions, there were also high concentrations of total PM10 Mo, Cr and As (Fig. 4) ~~(Fig. 4), and the enrichment factor of Cr was moderately enriched (EF of 4.2)~~. Small emissions of these three trace elements come from natural and anthropogenic sources (Lane et al., 2013;Pacyna and Nriagu, 1988). ~~such as mineral dust, or volcanic emissions in the case of As. The greatest anthropogenic As emissions come from pyrometallurgical operations in the production of nonferrous metals, combustion of fossil fuels and the use of pesticides. Anthropogenic sources of aerosol Mo include the erosion of vehicle parts (Lane et al., 2013), while anthropogenic Cr in the atmosphere is sourced from metallurgical and alloy steel, chemical, and refractory industry, coal and oil combustion, cement manufacturing, and refuse incineration (Pacyna and Nriagu, 1988).~~ Back trajectories passed over coastal regions of ~~Queensland~~moderate urban activity, i.e., trajectory type “b” (Fig. 1), suggesting that air masses could have contained a mixture of dust and minor anthropogenic derived aerosols.

4.5.3. Fire events

The discussion of aerosol Fe during fire events focusses on the three major events occurring on the 9 June (fire event “E”), 25 June (fire event “FG”) and 26-27 June 2014 (fire event “HI”) ~~2014~~ (~~[~~Mallet et al., submitted acp-2016-731~~in prep~~)~~]~~. ~~These events were comprised of C3 burning inferred from δ^{13}C in CO_2 during the campaign [Paton-Walsh et al. 2016], and aerosol mass concentrations were higher than usual for the campaign.~~ These events were identified from large enhancements in CO and aerosol mass concentrations over the usual levels for the campaign (Desservettaz et al, submitted acp-2016-708). Concentrations of non-refractory particulate matter less than 1 μm (PM1) increased up to 500 μg m^{-3} (~~[~~Mallet et al., submitted acp-2016-731~~*Mallet et al.*, in prep~~)~~]~~. During these fire events, total PM10 Fe (400-800 ng m^{-3}) and soluble Fe (7-66 ng m^{-3}) concentrations and fractional Fe solubility (~3 %) were considerably less than the average concentration and fractional solubility throughout the campaign. For the first half of the campaign, from~~ the~~ 4-20 June, fractional Fe solubility averaged 10 % and then dropped to ~3 % between 21-27 June. During the drop in fractional Fe solubility, soluble and total PM10 Fe concentrations were the lowest found throughout the campaign.

We compare the fractional Fe solubility to biomass burn~~r~~ing proxies during the campaign. There is no significant relationship between fractional Fe solubility and the biomass burning tracers (nss-K, elemental carbon, oxalate or levoglucosan) throughout campaign (~~; ~~Fig. S2). ~~However~~Nevertheless, fractional Fe solubility is typically ~~higher ~~lower when elemental carbon concentrations are ~~low ~~high~~and vice versa~~, excluding dust event “A” (r^2=0.33).~~ ~~ The period of low fractional Fe solubility ~3 %, between the 21-27 June, encompasses the ~~During the ~~exceptionally large fire events “FG” and “HI.” Biomass burning was most intense during this second half of the campaign. ~~, fractional Fe solubility was the lowest (~3 %). ~~In agreement with high concentrations of elemental carbon, oxalate and levoglucosan at this time, visual examination the aerosol filters showed that between the 21-27 June, filters were exceptionally caked with soot. The lowest fractional Fe solubility during fire event “FG” and “HI” is related to proximal fires, whilst the fractional Fe solubility was relatively high during fire event “E” when fires were distantly sourced. ~~(Milic et al., 2016)~~

4.6. Biomass burning derived soluble iron -~~–~~ combustion and transport

During the large burning events in this study, fresh elemental carbon is an insignificant source of soluble Fe to the aerosol; fresh elemental carbon has a relatively low Fe solubility, it is initially hydrophobic (see below) and it contains relatively little Fe. However, biomass burning can indirectly influence the fractional Fe solubility of aerosols through physical processes, such as the entrainment of local soil particles into the smoke plume, black carbon containing particles acting as a substrate for long-range aerosol Fe transport, and the bioavailability of nano-Fe. In addition, chemical processes, such as oxalate modification and aerosol aging, may also impact fractional Fe solubility in biomass burning plumes. The low fractional Fe solubility of ~3 % during periods of high elemental carbon, oxalate and levoglucosan concentrations could be related to the entrainment of fine soil parties into the smoke plume during intensive fires. The incorporation of local dust into the aerosol explains the low EFs and elevated nss-K ratios during the largest fire events. Back trajectories and radon also show that mineral dust was sourced from central Australian desert. The fractional Fe solubility at this time is similar to dust estimates around 0.5-2 % at relatively high Fe mass concentrations (Sholkovitz et al., 2012).

Iron can be bound to long-range transportable black carbon-containing particle aggregates deposited in Antarctic snow and ice (Ellis et al., 2015). Little is known about the process in which Fe is bound to black carbon-containing particle aggregates. Iron could originate from Fe contained within the biomass (Maenhaut et al., 2002;Yamasoe et al., 2000;Reid et al., 2005), local soil Fe incorporated into the aerosol mixture during combustion, or the binding of aerosol Fe to black carbon-containing particles in the atmosphere during transport. Using single particle analysis, mixed sources (e.g. black carbon and aluminosilicates) were detected in long-range transported aerosols to Antarctica (Ellis et al., 2015). It is not surprising that the fractional Fe solubility data (2-12 %) plots mid-range for aerosol Fe sources characteristic of dust and combustion in the Southern Hemisphere (Fig. 7).

~~Biomass burning is a potentially large source of soluble Fe to the open ocean (Guieu et al., 2005;Ito, 2015, 2013). Ito (2015) estimate that in the north Australian coastal region, biomass burning contributes around 60-70 % of the total soluble Fe deposition, where the dust contribution is less (40-50 %). Australia is one of the primary regions of biomass burning in the Southern Hemisphere (Giglio et al., 2013) and constitutes a large source of annual dry season aerosol emissions over northern Australia, and episodic austral summer wildfires in southern and eastern Australia (e.g. Meyer et al., 2008). Modelling by Ito (2015) suggests biomass burning derived soluble Fe contributes substantial inputs of soluble Fe to tropical and Southern Ocean waters downwind of Australia. Over the Southern Ocean, there is a larger contribution of biomass burning aerosol Fe than mineral dust and fossil fuel combustion derived aerosol Fe. Therefore biomass burning could be an important source of soluble Fe to both tropical and Southern Ocean waters surrounding Australia.~~

The particle size distribution of biomass burning aerosols was typically centred around 95 nm (with 95 % of all particles between 30-280 nm) for nearby fresh smoke at Gunn Point and around 120 nm (95 % of all particles were between 40-390 nm) for distant aged smoke at Gunn Point (~~[~~Mallet et al., submitted acp-2016-731~~*Mallet et al*., in prep~~)~~]~~. While the literature shows that for aged/long-range transported smoke, the particle size~~d~~ distribution ranges between 75-540 nm (Kipling et al., 2013). As the particle size distribution for black carbon is in the nanometre range, any Fe associated with black carbon-containing particles is operationally defined as soluble (i.e., <0.2 µm). The majority of soluble Fe in Gunn Point aerosols during large biomass burning events was within this~~e~~ <0.2 µm pool (i.e., the concentration of soluble Fe <0.2 µm was 7 ng m^{-3} compared to the bulk soluble Fe concentration of 10 ng m^{-3} in GP22). Leachates showed large variability in their colour, and visual observation after particle settling showed that leachates of biomass burning events ~~they~~ contained a large number of very fine particles in the <0.2 µm filtered fraction. PM1 ambient aerosols sampled during the SAFIRED campaign were dominated by an organic fraction (Milic et al., 2016). Many of the finer particles are also likely to be derived from biomass burning, given the particle size distribution of biomass burning aerosols at Gunn Point was typically centred around 100 nm (Mallet et al., submitted acp-2016-731) and thus operationally defined as soluble. Recent studies show that nanometre-sized Fe particles are potentially bioavailable (e.g. Raiswell et al., 2008).~~,~~ The proportion of soluble Fe in the <0.2 µm pool is likely to vary between the dry and wet season as different aerosol sources switch on and off, i.e., mineral dust has a courser particle size distribution than biomass burning derived particles. ~~and thus~~ F~~f~~uture work should be directed towards quantifying biomass burning sources of bioavailable Fe in tropical and remote oceanic regions.

~~Iron can be bound to long-range transportable black carbon-containing particle aggregates deposited in Antarctic snow and ice (Ellis et al., 2015). Little is known about the process in which Fe is bound to black carbon-containing particle aggregates, but Fe could originate from Fe contained within the biomass (Maenhaut et al., 2002;Yamasoe et al., 2000;Reid et al., 2005), soil Fe incorporated into the aerosol mixture during combustion, or the binding of aerosol Fe to black carbon-containing particles in the atmosphere during transport. Using single particle analysis, mixed sources (e.g. black carbon and aluminosilicates) were~~

~~detected in long-range transported aerosols to Antarctica (Ellis et al., 2015). It is not surprising that the fractional Fe solubility data (2-12 %) plots mid-range for aerosol Fe sources characteristic of dust and combustion in the Southern Hemisphere (Fig. 7).~~

~~Generally, the fractional Fe solubility was lower when fresh elemental carbon concentrations were high and sourced from proximal fires at Gunn Point (Fig. 6). This relationship could be related to the hydrophobic, i.e. water insoluble, nature of black carbon-containing particles in water (e.g. Chughtai et al., 1996). The low soluble Fe concentrations, and hence low fractional Fe solubility, derived from the heavily caked soot filters between the 21 and 27 June could reflect the physical properties of fresh black carbon, i.e., fresh black carbon does not disperse in water thus any soluble Fe associated with fresh black carbon is not dispersed in the water leach. However, combustion aerosols are known to have a high factional Fe solubility (Sholkovitz et al., 2012) and often these studies are based on aerosols collected shipboard in the remote open ocean where aerosol Fe has undergone atmospheric transport and aging. Therefore, the fractional Fe solubility in these studies is not directly comparable to fresh combustion Fe reported in this study. Combustion aerosols can become more soluble with transport (Ito, 2015). There is a growing body of work that suggests aerosol Fe solubility can be enhanced by cloud chemistry and acid processing (Meskhidze et al., 2003;Spokes et al., 1994;Desboeufs et al., 1999;Kumar et al., 2010;Hoffer et al., 2005). Ito and Shi (2016) show that enhanced Fe solubility of dust could be related to reactive organic species such as oxalate, in cloud water, which contains Fe-binding functionalities such as humic-like substances from biomass burning. Al-Abadleh (2015) (Al-Abadleh, 2015)Fresh black carbon-containing particles are initially insoluble, but can be aged into a form that disperses in water following uptake of sulphuric acid and secondary organic material via condensation and coagulation in the atmosphere. Black carbon particles can act as a seed for condensation and the components that condense on the surface of the black carbon particles are water soluble. Aged black carbon-containing particles can also disperse in water through the oxidation with functional groups during atmospheric transport over the remote ocean (Lohmann et al., 2000;Decesari et al., 2002;Chughtai et al., 1991;Chughtai et al., 1996). If the surface of black carbon particles becomes hydrophilic with the coating of water soluble species in the atmosphere, soluble Fe bound to the black carbon-containing particles would disperse in water and be captured in the water soluble Fe leach. This could explain why, i) the fractional Fe solubility was higher in distally sourced fire event "E" compared to proximal fire events "FG" and "HI", and ii) the relatively high fractional Fe solubility observed in long-range transported aerosol to the remote Southern Ocean and Antarctica (Conway et al., 2015;Gaspari et al., 2006;Winton et al., 2015;Winton et al., 2016b). The impact of transport time and distance on fractional Fe solubility should be further investigated. (Sholkovitz et al., 2012)~~

Oxalate modification of mineral dust could be a leading factor enhancing the fractional Fe solubility of mineral dust (Ito and Shi, 2016) in regions where there are high oxalate concentrations in the atmosphere, such as the tropics. The higher fractional Fe solubility during dust events compared to fire events at Gunn Point could be related to biomass burning derived-oxalate enhancing the solubility of Australian mineral dust that has been transported to the Northern Territory and mixed with biomass burning plumes (Fig. 6). The fractional Fe solubility of mineral dust in the Southern Hemisphere is around 0.5-2 % (Sholkovitz et al., 2012), which is lower than our estimates of fractional Fe solubility during dust events in northern Australia. Only trace concentrations of oxalate are found in air masses in lower latitudes over Antarctica and the Southern Ocean (Keywood, 2007). Although, little is known about the enhancement of fractional Fe solubility in these pristine air masses (Chance et al., 2015;Winton et al., 2015), the concentrations of oxalate could ~~well~~ be too low to influence fractional ~~iron~~Fe solubility of mineral dust. Therefore, the mean biomass burning enhanced mineral dust fractional Fe solubility of ~8 % represents an upper bound of mineral dust fractional Fe solubility in the Australian tropics during the dry season as illustrated in Fig. 7.

Despite the influx of aerosols from proximal fires, the fractional Fe solubility remained low between the 21 and 27 June (Fig. 6). This relationship could be related to the hydrophobic, i.e. water insoluble, nature of black carbon-containing particles in water (e.g. Chughtai et al., 1996). The low soluble Fe concentrations, and hence low fractional Fe solubility, derived from the heavily caked soot filters between the 21 and 27 June could reflect the physical properties of fresh black carbon, i.e., fresh black carbon does not disperse in water thus any soluble Fe associated with fresh black carbon is not incorporated into the water leach. However, combustion aerosols are known to have a high factional Fe solubility (Sholkovitz et al., 2012) and often these studies are based on aerosols collected shipboard in the remote open ocean where aerosol Fe has undergone atmospheric transport and aging. Therefore, the fractional Fe solubility in these studies is not directly comparable to fresh combustion Fe reported in this study. Combustion aerosols can become more soluble with transport (Ito, 2015). There is a growing body of work that suggests aerosol Fe solubility can be enhanced by cloud chemistry and acid processing (Meskhidze et al., 2003;Spokes et al., 1994;Desboeufs et al., 1999;Kumar et al., 2010;Hoffer et al., 2005). Ito and Shi (2016) show that enhanced Fe solubility of dust could be related to reactive organic species, such as oxalate, in cloud water, which contains Fe-binding functionalities such as humic-like substances from biomass burning. In a review of Fe chemistry in systems containing humic-like substances, Al-Abadleh (2015) highlights the complexation and dissolution processes in which aerosol Fe solubility is enhanced with organic compounds. Fresh black carbon-containing particles are initially insoluble, but can be aged into a form that disperses in water following uptake of sulphuric acid and secondary organic material via condensation and coagulation in the atmosphere. Black carbon particles can act as a seed for condensation and the components that condense on the surface of the black carbon particles are water soluble. Aged black carbon-containing particles can also disperse in water through the oxidation with functional groups during atmospheric transport over the remote ocean (Lohmann et al., 2000;Decesari et al., 2002;Chughtai et al., 1991;Chughtai et al., 1996). If the surface of black carbon particles becomes hydrophilic with a coating of water soluble species in the atmosphere, soluble Fe bound to the black carbon-containing particles would disperse in water and be captured in the water soluble Fe leach. There was no significant atmospheric processing of proximal fires during the SAFRIED campaign (Milic et al., 2016). The lack of atmospheric processing could explain why, i) the fractional Fe solubility was higher in distally sourced fire event “E” compared to proximal fire events “FG” and “HI”, and ii) the relatively high fractional Fe solubility observed in long-range transported aerosol to the remote Southern Ocean and Antarctica (Conway et al., 2015;Gaspari et al., 2006;Winton et al., 2015;Winton et al., 2016b). The impact of transport time and distance on fractional Fe solubility should be further investigated.

We provide evidence that Fe in freshly emitted biomass burning aerosols are not particularly soluble. In turn this suggests that atmospheric aging itself plays a significant role in observations of soluble Fe in plumes sampled far from combustion sources.

~~The relatively low fractional Fe solubility in mixed dust and fresh biomass burning aerosols at Gunn Point, compared to other estimates of combustion aerosols (up to 60 %), could be related to the short aging time of fresh biomass burning in our samples.~~ Ito (2015) model the transport of soluble Fe derived from combustion sources. The model indicates relatively low fractional Fe solubility near the sources of biomass burning and coal combustion. The fractional Fe solubility becomes higher as aerosols are transported to the open ocean. Therefore, transport time and distance could be an import factor in fractional Fe solubility. Alternatively, the relatively low fractional Fe solubility could be related to the type of biomass in northern Australia (i.e., savannah that is comprised of eucalypt dominated woodlands (10-30 % foliage cover) and open-forests (30-70 % foliage cover), with a diverse woody sub-canopy and grassy ground cover (Edwards et al., 2015)~~)~~. There is a wide range of fractional Fe solubility estimates for combustion aerosols in the literature and more studies are required to understand the fractional Fe solubility in different biomass types. On the other hand, low fractional Fe solubility during fire events~~ and the inverse relationship~~ ~~between elemental carbon and soluble Fe~~ questions whether biomass burning could be a potential bioavailable source of Fe. In a study of biomass burning-related emissions of Fe in the Mediterranean, Guieu et al. (2005) found that fractional Fe solubility was lower than this study (0.6 to 2 %) and concluded that while biomass burning may have a significant local effect on aerosol Fe supply to the ocean, on a global scale biomass burning has little impact. Clearly future work should be directed towards the solubility of Fe in fresh and aged smoke plumes. We have focused our discussion around the fractional Fe solubility of mixed biomass burning aerosols and mineral dust. The trends in fractional Fe solubility paralleled fractional Al and Ti (but not Mn) solubility variation throughout the campaign, implying that the factors that regulate fractional Fe solubility in these samples may also regulate the solubility of Al and Ti. Little is known about the fractional Al, Ti and Mn solubility in biomass burning aerosols future work. Again, future studies should investigate these Fe, Al and Ti aerosols in conjunction both at the source and in long range air masses downwind of biomass burning.

5. Conclusions

Co-emissions of mineral dust and aged biomass burning from Australia are potential sources of soluble Fe to ~~the Southern Ocean and~~ Australian tropical waters. During the SAFIRED campaign, northern Australia in the dry season 2014, there was considerable temporal variability in soluble and total PM10 aerosol Fe concentrations that reflect coincident mineral dust and fresh smoke sources. Fractional Fe solubility was relatively high throughout the campaign and ranged from 2 to 12 %. During dust events, the fractional Fe solubility was greatest (12 %), however, decreased to 3 % during an ~~extreme~~ intense biomass burning ~~event~~period. Whilst mineral dust supplied soluble ~~iron~~Fe throughout the campaign, the lower fractional Fe solubility in the large biomass burning event suggests that the primary factor controlling soluble ~~iron~~Fe was the presence of mineral dust. The dust could have been entrained into the biomass burning plume from local soil and also transported from central Australian desserts. Due to the hydrophobic nature of fresh black carbon, biomass burning ~~derived soluble iron~~ itself may not be a direct source of soluble ~~iron~~Fe to the ocean. Nevertheless, biomass burning species can enhance the soluble ~~iron~~ Fe chemistry in mixed aerosols. Iron in dust may be more soluble in the tropics, compared to higher latitudes, due to the higher concentrations of biomass burning derived reactive organic species in the atmosphere, such as oxalate, and their potential to enhance the fractional Fe solubility of mineral dust during transport. Soluble Fe could be further enhanced during atmospheric transport and aging of black carbon-containing particles that could explain the relatively high episodic fractional Fe solubility observed in long-range transportable aerosol Fe to the Southern Ocean and Antarctica. In addition, black carbon-containing particles can act as a surface for aerosol ~~iron~~Fe to bind to during transport. Biomass burning constitutes a large fraction of the aerosol loading over the tropics which has the potential to modulate soluble Fe and trigger nitrogen fixing toxic algal blooms. Such~~,~~ toxic algal blooms have harmful consequences for humans and other vertebrates. The understanding of the factors that initiate algal blooms needs to be improved (Law et al., 2011;Abram et al., 2003), especially over tropical regions where inputs of biomass burning to the ocean are predicted to increase over the next century (Keywood et al., 2013).

Data availability

The trace element dataset is available through the Curtin University Research Data repository http://doi.org/10.4225/06/5671012A48C2A.

Author contribution

V.H.L.W., R.E. and A.R.B. designed the research; V.H.L.W. and M.D. collected the aerosol filters; V.H.L.W., R.E. and A.R.B. prepared the trace element filter samples, analyzed and evaluated the data; P.W.S. prepared the elemental carbon and major ion filter samples and analyzed the data; M.D. and C.P.W. collected and analyzed the carbon monoxide data; S.C. and A.W. collected and analyzed the radon data; M.M and M.K. analyzed the particle size distribution data; M.K., P.W.S., S.C., A.W., M.M., M.D., C.P.W. and V.H.L.W. contributed to the field campaign; V.H.L.W. prepared the manuscript with contributions from all co-authors.

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References

Abram, N. J., Gagan, M. K., McCulloch, M. T., Chappell, J., and Hantoro, W. S.: Coral reef death during the 1997 Indian Ocean dipole linked to Indonesian wildfires, Science, 301, 952-955, 2003.

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.

Al-Abadleh, H. A.: Review of the bulk and surface chemistry of iron in atmospherically relevant systems containing humic-like substances, RSC Advances, 5, 45785-45811, 2015.

Andersen, A. N., Cook, G. D., Corbett, L. K., Douglas, M. M., Eager, R. W., RUSSELL-SMITH, J., Setterfield, S. A., Williams, R. J., and Woinarski, J. C.: Fire frequency and biodiversity conservation in Australian tropical savannas: implications from the Kapalga fire experiment, Austral Ecology, 30, 155-167, 2005.

Andreae, M., and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmospheric Chemistry and Physics, 6, 3131-3148, 2006.

Arimoto, R., Duce, R. A., and Ray, B. J.: Concentrations, sources and air-sea exchange of trace elements in the atmosphere over the Pacific Ocean, Chemical Oceanography, 10, 107-149, 1989.

Baker, A., Kelly, S., Biswas, K., Witt, M., and Jickells, T.: Atmospheric deposition of nutrients to the Atlantic Ocean, Geophysical Research Letters, 30, 2003.

Baker, A., Weston, K., Kelly, S., Voss, M., Streu, P., and Cape, J.: Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation, Deep Sea Research Part I: Oceanographic Research Papers, 54, 1704-1720, 2007.

Baker, A., Adams, C., Bell, T., Jickells, T., and Ganzeveld, L.: Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50° N to 50° S based on large-scale field sampling: Iron and other dust-associated elements, Global Biogeochemical Cycles, 27, 755-767, 2013.

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.

Baker, A. R., and Croot, P. L.: Atmospheric and marine controls on aerosol iron solubility in seawater, Marine Chemistry, 120, 4-13, 2010.

Berman-Frank, I., Cullen, J. T., Shaked, Y., Sherrell, R. M., and Falkowski, P. G.: Iron availability, cellular iron quotas, and nitrogen fixation in Trichodesmium, Limnology and Oceanography, 46, 1249-1260, 2001.

Bisiaux, M., Edwards, R., McConnell, J., Curran, M., Van Ommen, T., Smith, A., Neumann, T., Pasteris, D., Penner, J., and Taylor, K.: Changes in black carbon deposition to Antarctica from two high-resolution ice core records, 1850–2000 AD, Atmospheric Chemistry and Physics, 12, 4107-4115, 2012.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, Journal of Geophysical Research: Atmospheres, 118, 5380-5552, 10.1002/jgrd.50171, 2013.

Bowie, A. R., Lannuzel, D., Remenyi, T. A., Wagener, T., Lam, P. J., Boyd, P. W., Guieu, C., Townsend, A. T., and Trull, T. W.: Biogeochemical iron budgets of the Southern Ocean south of Australia: Decoupling of iron and nutrient cycles in the subantarctic zone by the summertime supply, Global Biogeochem. Cycles, 23, GB4034, 10.1029/2009gb003500, 2009.

Bowler, J.: Aridity in Australia: age, origins and expression in aeolian landforms and sediments, Earth-Science Reviews, 12, 279-310, 1976.

Boyd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R., Bakker, D. C. E., Bowie, A. R., Buesseler, K. O., Chang, H., Charette, M., Croot, P. L., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M. I., Ling, R., Maldonado, M. T., McKay, R. M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., and Zeldis, J.: A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, Nature, 407, 695-702, 2000.

Boyd, P. W., and Ellwood, M. J.: The biogeochemical cycle of iron in the ocean, Nature Geosci, 3, 675-682, http://www.nature.com/ngeo/journal/v3/n10/abs/ngeo964.html#supplementary-information, 2010.

Carslaw, D. C., and Ropkins, K.: Openair - An R package for air quality data analysis, Environmental Modelling & Software, 27, 52-61, 2012.

Carslaw, D. C.: The openair manual - open-source tools for analysing air pollution data., Manual for version 1.0, King's College London., 2014.

Chambers, S., Hong, S.-B., Williams, A., Crawford, J., Griffiths, A., and Park, S.-J.: Characterising terrestrial influences on Antarctic air masses using Radon-222 measurements at King George Island, Atmospheric Chemistry and Physics, 14, 9903-9916, 2014.

Chambers, S., Williams, A., Crawford, J., and Griffiths, A.: On the use of radon for quantifying the effects of atmospheric stability on urban emissions, Atmospheric Chemistry and Physics, 15, 1175-1190, 2015.

Chance, R., Jickells, T. D., and Baker, A. R.: Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic, Marine Chemistry, 2015.

Chow, J. C., Watson, J. G., Chen, L.-W. A., Chang, M. O., Robinson, N. F., Trimble, D., and Kohl, S.: The IMPROVE_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database, Journal of the Air & Waste Management Association, 57, 1014-1023, 2007.

Chuang, P. Y., Duvall, R. M., Shafer, M. M., and Schauer, J. J.: The origin of water soluble particulate iron in the Asian atmospheric outflow, Geophys. Res. Lett., 32, L07813, 10.1029/2004gl021946, 2005.

Chughtai, A., Jassim, J., Peterson, J., Stedman, D., and Smith, D.: Spectroscopic and solubility characteristics of oxidized soots, Aerosol Science and Technology, 15, 112-126, 1991.

Chughtai, A., Brooks, M., and Smith, D.: Hydration of black carbon, Journal of Geophysical Research: Atmospheres (1984–2012), 101, 19505-19514, 1996.

Conway, T., Wolff, E., Röthlisberger, R., Mulvaney, R., and Elderfield, H.: Constraints on soluble aerosol iron flux to the Southern Ocean at the Last Glacial Maximum, Nature Communications, 6, 2015.

Cropp, R. A., Gabric, A. J., Levasseur, M., McTainsh, G. H., Bowie, A., Hassler, C. S., Law, C. S., McGowan, H., Tindale, N., and Viscarra Rossel, R.: The likelihood of observing dust-stimulated phytoplankton growth in waters proximal to the Australian continent, Journal of Marine Systems, 117–118, 43-52, http://dx.doi.org/10.1016/j.jmarsys.2013.02.013, 2013.

Cutter, G., Andersson, P., Codispoti, L., Croot, P., Francois, R., Lohan, M., Obata, H., and Rutgers vd Loeff, M.: Sampling and sample-handling protocols for GEOTRACES Cruises, 2010.

De Deckker, P., Norman, M., Goodwin, I. D., Wain, A., and Gingele, F. X.: Lead isotopic evidence for an Australian source of aeolian dust to Antarctica at times over the last 170,000 years, Palaeogeography, Palaeoclimatology, Palaeoecology, 285, 205-223, 2010.

Decesari, S., Facchini, M., Matta, E., Mircea, M., Fuzzi, S., Chughtai, A., and Smith, D.: Water soluble organic compounds formed by oxidation of soot, Atmospheric Environment, 36, 1827-1832, 2002.

Desboeufs, K., Losno, R., Vimeux, F., and Cholbi, S.: The pH-dependent dissolution of wind-transported Saharan dust, Journal of Geophysical Research: Atmospheres (1984–2012), 104, 21287-21299, 1999.

Dörr, H., Kromer, B., Levin, I., Münnich, K., and Volpp, H. J.: CO2 and Radon 222 as tracers for atmospheric transport, Journal of Geophysical Research: Oceans (1978–2012), 88, 1309-1313, 1983.

Draxler, R. R., and Rolph, G. D.: Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT), model, http://www.arl.noaa.gov/ready/hysplit4.html, 2003.

Duce, R., Arimoto, R., Ray, B., Unni, C., and Harder, P.: Atmospheric trace elements at Enewetak Atoll: 1. Concentrations, sources, and temporal variability, Journal of Geophysical Research: Oceans, 88, 5321-5342, 1983.

Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., Buat-Menard, P., Hicks, B. B., Miller, J. M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L., Jickells, T. D., Knap, A. H., Reinhardt, K. H., Schneider, B., Soudine, A., Tokos, J. J., Tsunogai, S., Wollast, R., and Zhou, M.: The atmospheric input of trace species to the world ocean, Global Biogeochem. Cycles, 5, 193-259, 10.1029/91gb01778, 1991.

Edwards, A., Russell-Smith, J., and Meyer, M.: Contemporary fire regime risks to key ecological assets and processes in north Australian savannas, International Journal of Wildland Fire, 24, 857-870, 2015.

Ellis, A., Edwards, R., Saunders, M., Chakrabarty, R. K., Subramanian, R., van Riessen, A., Smith, A. M., Lambrinidis, D., Nunes, L. J., Vallelonga, P., Goodwin, I. D., Moy, A. D., Curran, M. A. J., and van Ommen, T. D.: Characterizing black carbon in rain and ice cores using coupled tangential flow filtration and transmission electron microscopy, Atmos. Meas. Tech., 8, 3959-3969, 10.5194/amt-8-3959-2015, 2015.

Elrod, V., Berelson, W., Coale, K., and Johnson, K.: The flux of iron from continental shelf sediments: a missing source for global budgets, Geophys Res Lett, 31, L12307, 2004.

Falkowski, P. G.: Evolution of the nitrogen cycle and its influence on the biological sequestration of CO 2 in the ocean, Nature, 387, 272-275, 1997.

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.

Gabric, A. J., Cropp, R. A., McTainsh, G. H., Johnston, B. M., Butler, H., Tilbrook, B., and Keywood, M.: Australian dust storms in 2002–2003 and their impact on Southern Ocean biogeochemistry, Global Biogeochemical Cycles, 24, 2010.

Gao, Y., Xu, G., Zhan, J., Zhang, J., Li, W., Lin, Q., Chen, L., and Lin, H.: Spatial and particle size distributions of atmospheric dissolvable iron in aerosols and its input to the Southern Ocean and coastal East Antarctica, Journal of Geophysical Research: Atmospheres, 118, 12,634-612,648, 2013.

Garcia, N. S., Fu, F., Sedwick, P. N., and Hutchins, D. A.: Iron deficiency increases growth and nitrogen-fixation rates of phosphorus-deficient marine cyanobacteria, ISME J, 9, 238-245, 10.1038/ismej.2014.104, 2015.

Gaspari, V., Barbante, C., Cozzi, G., Cescon, P., Boutron, C. F., Gabrielli, P., Capodaglio, G., Ferrari, C., Petit, J. R., and Delmonte, B.: Atmospheric iron fluxes over the last deglaciation: Climatic implications, Geophys. Res. Lett., 33, L03704, 10.1029/2005gl024352, 2006.

Gelado-Caballero, M. D., López-García, P., Prieto, S., Patey, M. D., Collado, C., and Hérnández-Brito, J. J.: Long-term aerosol measurements in Gran Canaria, Canary Islands: Particle concentration, sources and elemental composition, Journal of Geophysical Research: Atmospheres, 117, 2012.

Giglio, L., Randerson, J. T., and Werf, G. R.: Analysis of daily, monthly, and annual burned area using the fourth-generation global fire emissions database (GFED4), Journal of Geophysical Research: Biogeosciences, 118, 317-328, 2013.

Guieu, C., Bonnet, S., Wagener, T., and Loÿe-Pilot, M. D.: Biomass burning as a source of dissolved iron to the open ocean?, Geophysical Research Letters, 32, 2005.

Hesse, P. P.: The record of continental dust from Australia in Tasman Sea sediments, Quaternary Science Reviews, 13, 257-272, 1994.

Hesse, P. P., and McTainsh, G. H.: Australian dust deposits: modern processes and the Quaternary record, Quaternary Science Reviews, 22, 2007-2035, 2003.

Hibberd, M., Selleck, P., Keywood, M., Cohen, D., Stelcer, E., and Atanacio, A.: Upper Hunter Particle Characterisation Study, Australia: CSIRO, 2013.

Hoffer, A., Gelencsér, A., Guyon, P., Kiss, G., Schmid, O., Frank, G., Artaxo, P., and Andreae, M.: Optical properties of humiclike substances (HULIS) in biomass-burning aerosols, Atmos. Chem. Phys. Discuss, 5, 7341-7360, 2005.

Iinuma, Y., Engling, G., Puxbaum, H., and Herrmann, H.: A highly resolved anion-exchange chromatographic method for determination of saccharidic tracers for biomass combustion and primary bio-particles in atmospheric aerosol, Atmospheric Environment, 43, 1367-1371, 2009.

Ito, A.: Mega fire emissions in Siberia: potential supply of bioavailable iron from forests to the ocean, Biogeosciences, 8, 2011.

Ito, A.: Global modeling study of potentially bioavailable iron input from shipboard aerosol sources to the ocean, Global Biogeochemical Cycles, 27, 1-10, 2013.

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.

Johnson, K. S., Gordon, R. M., and Coale, K. H.: What controls dissolved iron concentrations in the world ocean?, Marine Chemistry, 57, 137-161, 1997.

Johnston, S. W.: The influence of aeolian dust deposits on alpine soils in south-eastern Australia, Soil Research, 39, 81-88, 2001.

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.

Keywood, M., Kanakidou, M., Stohl, A., Dentener, F., Grassi, G., Meyer, C., Torseth, K., Edwards, D., Thompson, A. M., and Lohmann, U.: Fire in the air: biomass burning impacts in a changing climate, Critical Reviews in Environmental Science and Technology, 43, 40-83, 2013.

Keywood, M. D.: Aerosol composition at Cape Grim : an evaluation of PM10 sampling program and baseline event switches., Baseline Atmospheric Program Australia 2005-2006. 2005-2006 ed. J. M. Cainey, N. Derek, and P. B. Krummel (editors). Melbourne: Australian Bureau of Meteorology and CSIRO Marine and Atmospheric Research, 31-36, 2007.

Kipling, Z., Stier, P., Schwarz, J., Perring, A., Spackman, J., Mann, G., Johnson, C., and Telford, P.: Constraints on aerosol processes in climate models from vertically-resolved aircraft observations of black carbon, Atmospheric Chemistry and Physics, 13, 5969, 2013.

Knapp, A. N., Casciotti, K. L., Berelson, W. M., Prokopenko, M. G., and Capone, D. G.: Low rates of nitrogen fixation in eastern tropical South Pacific surface waters, Proceedings of the National Academy of Sciences, 113, 4398-4403, 10.1073/pnas.1515641113, 2016.

Kumar, A., Sarin, M., and Srinivas, B.: Aerosol iron solubility over Bay of Bengal: Role of anthropogenic sources and chemical processing, Marine Chemistry, 121, 167-175, 2010.

Kustka, A. B., Sañudo-Wilhelmy, S. A., Carpenter, E. J., Capone, D., Burns, J., and Sunda, W. G.: Iron requirements for dinitrogen-and ammonium-supported growth in cultures of Trichodesmium (IMS 101): Comparison with nitrogen fixation rates and iron: Carbon ratios of field populations, Limnology and Oceanography, 48, 1869-1884, 2003.

Lane, S., Proemse, B. C., Tennant, A., and Wieser, M. E.: Concentration measurements and isotopic composition of airborne molybdenum collected in an urban environment, Analytical and bioanalytical chemistry, 405, 2957-2963, 2013.

LaRoche, J., and Breitbarth, E.: Importance of the diazotrophs as a source of new nitrogen in the ocean, Journal of Sea Research, 53, 67-91, 2005.

Law, C., Woodward, E., Ellwood, M., Marriner, A., Bury, S., and Safi, K.: Response of surface nutrient inventories and nitrogen fixation to a tropical cyclone in the southwest Pacific, Limnology and Oceanography, 56, 1372-1385, 2011.

Lenes, J., Darrow, B., Walsh, J., Prospero, J., He, R., Weisberg, R., Vargo, G., and Heil, C.: Saharan dust and phosphatic fidelity: A three-dimensional biogeochemical model of Trichodesmium as a nutrient source for red tides on the West Florida Shelf, Continental Shelf Research, 28, 1091-1115, 2008.

Lohmann, U., Feichter, J., Penner, J., and Leaitch, R.: Indirect effect of sulfate and carbonaceous aerosols- A mechanistic treatment, Journal of Geophysical Research, 105, 12193-12206, 2000.

Mackie, D. S., Boyd, P. W., Hunter, K. A., and McTainsh, G. H.: Simulating the cloud processing of iron in Australian dust: pH and dust concentration, Geophys. Res. Lett., 32, L06809, 10.1029/2004gl022122, 2005.

Mackie, D. S., Boyd, P. W., McTainsh, G. H., Tindale, N. W., Westberry, T. K., and Hunter, K. A.: Biogeochemistry of iron in Australian dust: From eolian uplift to marine uptake, Geochem. Geophys. Geosyst., 9, Q03Q08, 10.1029/2007gc001813, 2008.

Maenhaut, W., Fernández-Jiménez, M.-T., Rajta, I., and Artaxo, P.: Two-year study of atmospheric aerosols in Alta Floresta, Brazil: Multielemental composition and source apportionment, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 189, 243-248, 2002.

Mahowald, N. M., Baker, A. R., Bergametti, G., Brooks, N., Duce, R. A., Jickells, T. D., Kubilay, N., Prospero, J. M., and Tegen, I.: Atmospheric global dust cycle and iron inputs to the ocean, Global Biogeochem. Cycles, 19, GB4025, 10.1029/2004gb002402, 2005.

Mahowald, N. M., Engelstaedter, S., Luo, C., Sealy, A., Artaxo, P., Benitez-Nelson, C., Bonnet, S., Chen, Y., Chuang, P. Y., and Cohen, D. D.: Atmospheric iron deposition: Global distribution, variability, and human perturbations*, Marine Science, 1, 2009.

Marx, S. K., Kamber, B. S., and McGowan, H. A.: Estimates of Australian dust flux into New Zealand: Quantifying the eastern Australian dust plume pathway using trace element calibrated< sup> 210</sup> Pb as a monitor, Earth and Planetary Science Letters, 239, 336-351, 2005.

McTainsh, G., Chan, Y.-c., McGowan, H., Leys, J., and Tews, K.: The 23rd October 2002 dust storm in eastern Australia: characteristics and meteorological conditions, Atmospheric Environment, 39, 1227-1236, 2005.

Meskhidze, N., Chameides, W., Nenes, A., and Chen, G.: Iron mobilization in mineral dust: Can anthropogenic SO2 emissions affect ocean productivity?, Geophysical Research Letters, 30, 2003.

Meskhidze, N., Johnson, M. S., Hurley, D., and Dawson, K.: Influence of measurement uncertainties on fractional solubility of iron in mineral aerosols over the oceans, Aeolian Research, 22, 85-92, 2016.

Meyer, C. P., Luhar, A. K., and Mitchell, R. M.: Biomass burning emissions over northern Australia constrained by aerosol measurements: I—Modelling the distribution of hourly emissions, Atmospheric Environment, 42, 1629-1646, http://dx.doi.org/10.1016/j.atmosenv.2007.10.089, 2008.

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.

Mills, M. M., Ridame, C., Davey, M., La Roche, J., and Geider, R. J.: Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, Nature, 429, 292-294, 2004.

Morton, P. L., Landing, W. M., Hsu, S.-C., Milne, A., Aguilar-Islas, A. M., Baker, A. R., Bowie, A. R., Buck, C. S., Gao, Y., and Gichuki, S.: Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment, Limnology and Oceanography: Methods, 11, 62-78, 2013.

Pacyna, J., and Nriagu, J.: Atmospheric emissions of chromium from natural and anthropogenic sources, Chromium in the Natural and Human Environments, 105-123, 1988.

Paerl, H. W., Crocker, K. M., and Prufert, L. E.: Limitation of N2 fixation in coastal marine waters: Relative importance of molybdenum, iron, phosphorus, and organic matter availability1, Limnology and Oceanography, 32, 525-536, 1987.

Paerl, H. W., Prufert-Bebout, L. E., and Guo, C.: Iron-stimulated N2 fixation and growth in natural and cultured populations of the planktonic marine cyanobacteria Trichodesmium spp, Applied and Environmental Microbiology, 60, 1044-1047, 1994.

Paris, R., Desboeufs, K., Formenti, P., Nava, S., and Chou, C.: Chemical characterisation of iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX: implication for iron solubility, Atmospheric Chemistry and Physics, 10, 4273-4282, 2010.

Petzold, A., Ogren, J., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., and Sugimoto, N.: Recommendations for reporting" black carbon" measurements, Atmospheric Chemistry and Physics, 13, 8365-8379, 2013.

Raiswell, R., Benning, L. G., Davidson, L., and Tranter, M.: Nanoparticulate bioavailable iron minerals in icebergs and glaciers, Mineral Mag, 72, 345-348, 10.1180/minmag.2008.072.1.345, 2008.

Reid, J., Koppmann, R., Eck, T., and Eleuterio, D.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, Atmospheric Chemistry and Physics, 5, 799-825, 2005.

Reimann, C., and Caritat, P. d.: Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry, Environmental Science & Technology, 34, 5084-5091, 2000.

Revel-Rolland, M., De Deckker, P., Delmonte, B., Hesse, P. P., Magee, J. W., Basile-Doelsch, I., Grousset, F., and Bosch, D.: Eastern Australia: A possible source of dust in East Antarctica interglacial ice, Earth and Planetary Science Letters, 249, 1-13, 2006.

Rubin, M., Berman-Frank, I., and Shaked, Y.: Dust-and mineral-iron utilization by the marine dinitrogen-fixer Trichodesmium, Nature Geoscience, 4, 529-534, 2011.

Rueter, J. G.: Iron stimulation of photosynthesis and nitrogen fixation in anabaena 7120 and trichodesmium (cyanophyceae), Journal of Phycology, 24, 249-254, 1988.

Rueter, J. G., Hutchins, D. A., Smith, R. W., and Unsworth, N. L.: Iron nutrition of Trichodesmium, in: Marine pelagic cyanobacteria: Trichodesmium and other Diazotrophs, Springer, 289-306, 1992.

Schroth, A. W., Crusius, J., Sholkovitz, E. R., and Bostick, B. C.: Iron solubility driven by speciation in dust sources to the ocean, Nature Geosci, 2, 337-340, http://www.nature.com/ngeo/journal/v2/n5/suppinfo/ngeo501_S1.html, 2009.

Sedwick, P. N., Sholkovitz, E. R., and Church, T. M.: Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea, Geochem. Geophys. Geosyst., 8, Q10Q06, 10.1029/2007gc001586, 2007.

Shaw, E. C., Gabric, A. J., and McTainsh, G. H.: Impacts of aeolian dust deposition on phytoplankton dynamics in Queensland coastal waters, Marine and Freshwater Research, 59, 951-962, 2008.

Sholkovitz, E. R., Sedwick, P. N., Church, T. M., Baker, A. R., and Powell, C. F.: Fractional solubility of aerosol iron: Synthesis of a global-scale data set, Geochimica et cosmochimica acta, 89, 173-189, 2012.

Spokes, L. J., Jickells, T. D., and Lim, B.: Solubilisation of aerosol trace metals by cloud processing: A laboratory study, Geochimica et Cosmochimica Acta, 58, 3281-3287, 1994.

Sprigg, R.: Some stratigraphic consequences of fluctuating Quaternary sea levels and related wind regimes in southern and central Australia, Quarternary dust mantles, China New Zealand and Australia. Australian National University, Canberra, 211-240, 1982.

Srinivas, B., Sarin, M., and Kumar, A.: Impact of anthropogenic sources on aerosol iron solubility over the Bay of Bengal and the Arabian Sea, Biogeochemistry, 110, 257-268, 2012.

Tagliabue, A., Bopp, L., Dutay, J.-C., Bowie, A. R., Chever, F., Jean-Baptiste, P., Bucciarelli, E., Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., and Jeandel, C.: Hydrothermal contribution to the oceanic dissolved iron inventory, Nature Geosci, 3, 252-256, http://www.nature.com/ngeo/journal/v3/n4/suppinfo/ngeo818_S1.html, 2010.

Wagener, T., Guieu, C., Losno, R., Bonnet, S., and Mahowald, N.: Revisiting atmospheric dust export to the Southern Hemisphere ocean: Biogeochemical implications, Global Biogeochem. Cycles, 22, GB2006, 10.1029/2007gb002984, 2008.

Walsh, J. J., and Steidinger, K. A.: Saharan dust and Florida red tides: the cyanophyte connection, Journal of Geophysical Research: Oceans (1978–2012), 106, 11597-11612, 2001.

Wedepohl, K. H.: The composition of the continental crust, Geochimica et Cosmochimica Acta, 59, 1217-1232, 1995.

Whittlestone, S., and Zahorowski, W.: Baseline radon detectors for shipboard use: Development and deployment in the First Aerosol Characterization Experiment (ACE 1), Journal of Geophysical Research: Atmospheres (1984–2012), 103, 16743-16751, 1998.

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, 2016a.

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.

Winton, V. H. L., Edwards, R., Delmonte, B., Ellis, A., Andersson, P. S., Bowie, A., Bertler, N. A. N., Neff, P., and Tuohy, A.: Multiple sources of soluble atmospheric iron to Antarctic waters, Global Biogeochemical Cycles, 30, 421-437, 10.1002/2015GB005265, 2016b.

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.

Yamasoe, M. A., Artaxo, P., Miguel, A. H., and Allen, A. G.: Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements, Atmospheric Environment, 34, 1641-1653, 2000.

~~Table 1:Trace metal aerosol samples (PM10) collected at Gunn Point, dry season 2014.~~

~~Sample time~~	[a]~~Start date/ time~~	[a]~~Finish date/ time~~	~~Total sampling duration (min)~~	[b]~~Total air volume (m^3)~~	[c]~~Total air volume (m^3)~~
~~GP1~~	~~4/06/2014 11:05~~	~~5/06/2014 10:45~~	~~1117~~	~~1102~~	~~1122~~
~~GP2~~	~~5/06/2014 11:10~~	~~6/06/2014 12:30~~	~~1498~~	~~1458~~	~~1490~~
~~GP3~~	~~6/06/2014 12:55~~	~~7/06/2014 11:30~~	~~1355~~	~~1531~~	~~1572~~
~~GP4~~	~~7/06/2014 11:54~~	~~8/06/2014 8:47~~	~~1253~~	~~1416~~	~~1445~~
~~GP5~~	~~8/06/2014 9:08~~	~~9/06/2014 10:21~~	~~1512~~	~~1708~~	~~1715~~
~~GP6~~	~~9/06/2014 10:42~~	[d]~~10/06/2014~~	~~711~~	~~802~~	~~806~~
~~GP7~~	~~10/06/2014 2:41~~	~~11/06/2014 9:25~~	~~1112~~	~~1256~~	~~1278~~
~~GP8~~	~~11/06/2014 10:16~~	~~12/06/2014 10:43~~	~~1467~~	~~1658~~	~~1669~~
~~GP9~~	~~12/06/2014 11:03~~	~~13/06/2014 9:04~~	~~1322~~	~~1494~~	~~1518~~
~~GP10~~	~~13/06/2014 10:02~~	~~14/06/2014 10:56~~	~~1494~~	~~1688~~	~~1729~~
~~GP11~~	~~14/06/2014 11:31~~	~~15/06/2014 10:29~~	~~1378~~	~~1556~~	~~1584~~
~~GP12~~	~~15/06/2014 11:11~~	~~16/06/2014 10:16~~	~~1385~~	~~1565~~	~~1572~~
~~GP13~~	~~16/05/2014 10:45~~	~~17/06/2014 9:39~~	~~1374~~	~~1552~~	~~1550~~
~~GP14~~	~~17/06/2014 10:04~~	~~18/06/2014 10:18~~	~~1454~~	~~1643~~	~~1635~~
~~GP14~~	~~17/06/2014 10:04~~	~~18/06/2014 10:18~~	~~1454~~	~~1643~~	~~1635~~
~~GP15~~	~~18/06/2014 11:16~~	~~19/06/2014 10:15~~	~~1379~~	~~1559~~	~~1577~~
~~GP16~~	~~19/06/2014 10:41~~	~~20/06/2014 9:36~~	~~1375~~	~~1554~~	~~1584~~
~~GP17~~	~~20/06/2014 9:59~~	~~21/06/2014 9:58~~	~~1439~~	~~1626~~	~~1647~~
~~GP18~~	~~21/06/2014 10:31~~	~~22/06/2014 8:31~~	~~1319~~	~~1490~~	~~1508~~
~~GP19~~	~~22/06/2014 8:55~~	~~23/06/2014 9:32~~	~~1476~~	~~1668~~	~~1669~~
~~GP20~~	~~23/06/2014 10:39~~	~~24/06/2014 9:37~~	[c]~~1269~~	~~1429~~	~~1441~~
~~GP21~~	~~24/06/2014 10:04~~	~~25/06/2014 9:11~~	~~1387~~	~~1567~~	~~1569~~
~~GP22~~	~~25/06/2014 9:42~~	~~26/06/2014 9:05~~	~~1403~~	~~1499~~	~~1497~~
~~GP23~~	~~26/06/2014 9:46~~	~~27/06/2014 8:27~~	~~1360~~	~~1537~~	~~1536~~

[a] ~~Australian Central Standard Time~~

[b] ~~Total air volume calculated using STP.~~

[c] ~~Total air volume corrected to ambient temperature and pressure.~~

[d] ~~Fuse blown.~~

Table ~~2~~1: Aerosol iron concentrations and dry deposition fluxes for Gunn Point PM10 aerosols.

Sample	Soluble Fe concentration (ng m^{-3})	±	*Soluble Fe flux (µmol m^{-2} d^{-1})	±	Total Fe concentration (ng m^{-3})	±	*Total Fe flux (µmol m^{-2} d^{-1})	±
GP1	30	2	0.9	1.9~~0.5~~	286	9	9	18~~4~~
GP2	37	1	1.1	2.3~~0.6~~	384	12	12	24~~6~~
GP3	49	2	1.5	3.1~~0.8~~	598	19	18	37~~9~~
GP4	78	3	2.4	4.8~~1.2~~	1164	37	36	72~~18~~
GP5	140	6	4.3	8.7~~3.2~~	1158	37	36	71~~18~~
GP6	66	3	2.0	4.1~~1.0~~	823	26	25	51~~13~~
GP7	20	0.8	0.6	1.2~~0.3~~	236	7	7	15~~4~~
GP8	35	1	1.1	2.2~~0.5~~	374	12	12	23~~6~~
GP9	35	1	1.1	2.2~~0.5~~	385	12	12	24~~6~~
GP10	46	2	1.4	2.8~~0.7~~	539	17	17	33~~8~~
GP11	92	4	2.8	5.7~~1.4~~	928	29	29	57~~14~~
GP12	52	2	1.6	3.2~~0.8~~	677	21	21	42~~10~~
GP13	31	1	1.0	1.9~~0.5~~	331	10	10	20~~5~~
GP14	23	0.9	0.7	1.4~~0.3~~	192	6	6	12~~3~~
GP15	15	0.6	0.5	0.9~~0.2~~	123	4	4	8~~2~~
GP16	7	0.3	0.2	0.5~~.1~~	60	2	2	4~~1~~
GP17	67	3	2.1	4.2~~1.0~~	1129	36	35	70~~17~~
GP18	13	0.5	0.4	0.8~~2~~	247	8	8	15~~4~~
GP19	7	0.3	0.2	0.4~~0.1~~	231	7	7	14
GP20	13	0.5	0.4	0.8~~2~~	301	10	9	19~~5~~
GP21	7	0.3	0.2	0.5~~1~~	225	7	7	14~~3~~
GP22	10	0.4	0.3	0.6~~1~~	399	13	12	25~~6~~
GP23	11	0.4	0.3	0.7~~1~~	314	10	10	19~~5~~

*The uncertainty in dry deposition fluxes was calculated by propagation of error of the analytical uncertainty and uncertainty in the deposition velocity which is assumed to be a factor of 2-3 (Baker et al., 2003;Duce et al., 1991).~~was calculation by propagation of error of the analytical uncertainty and uncertainty in the deposition velocity assumed to be 50 %~~

Table ~~3~~2: Enrichment factor analysis of Gunn Point aerosol samples.

	Pb	Al	V	Cr	Mn	Fe	K
GP1	2.57	0.60	1.81	1.22	0.53	1.12	1.72
GP2	3.18	0.76	2.24	1.54	0.67	1.28	1.91
GP3	2.32	0.68	2.09	1.41	0.88	1.13	1.23
GP4	1.38	0.64	1.93	1.26	0.88	1.07	0.67
GP5	1.83	0.55	1.77	1.28	0.68	0.97	0.64
GP6	3.42	0.59	1.72	1.34	1.03	1.03	2.17
GP7	8.81	0.59	1.81	1.88	1.44	1.02	5.50
GP8	3.77	0.66	2.08	1.34	0.72	1.15	1.49
GP9	4.25	0.58	1.85	1.38	0.60	1.08	1.63
GP10	3.42	0.67	2.29	7.93	0.49	1.16	1.37
GP11	1.22	0.73	2.00	1.32	0.44	1.14	0.34
GP12	2.05	0.64	1.95	1.48	1.47	1.14	1.23
GP13	5.32	0.62	1.57	1.09	1.22	1.07	1.07
GP14	6.55	0.64	1.67	1.16	1.48	1.08	2.30
GP15	6.60	0.65	2.84	3.37	1.07	0.99	1.79
GP16	2.39	0.62	1.77	0.99	1.40	0.88	1.49
GP17	0.79	0.72	1.73	4.22	0.23	0.91	0.25
GP18	1.63	0.67	2.09	1.34	0.52	1.04	0.48
GP19	12.46	0.63	1.78	1.55	1.22	1.00	2.65
GP20	8.05	0.68	1.60	1.25	4.70	1.10	4.79
GP21	4.65	0.69	1.90	1.32	1.43	1.16	2.63
GP22	5.72	0.71	1.96	1.37	2.18	1.12	3.92
GP23	4.25	0.69	1.92	1.22	1.77	1.04	1.76

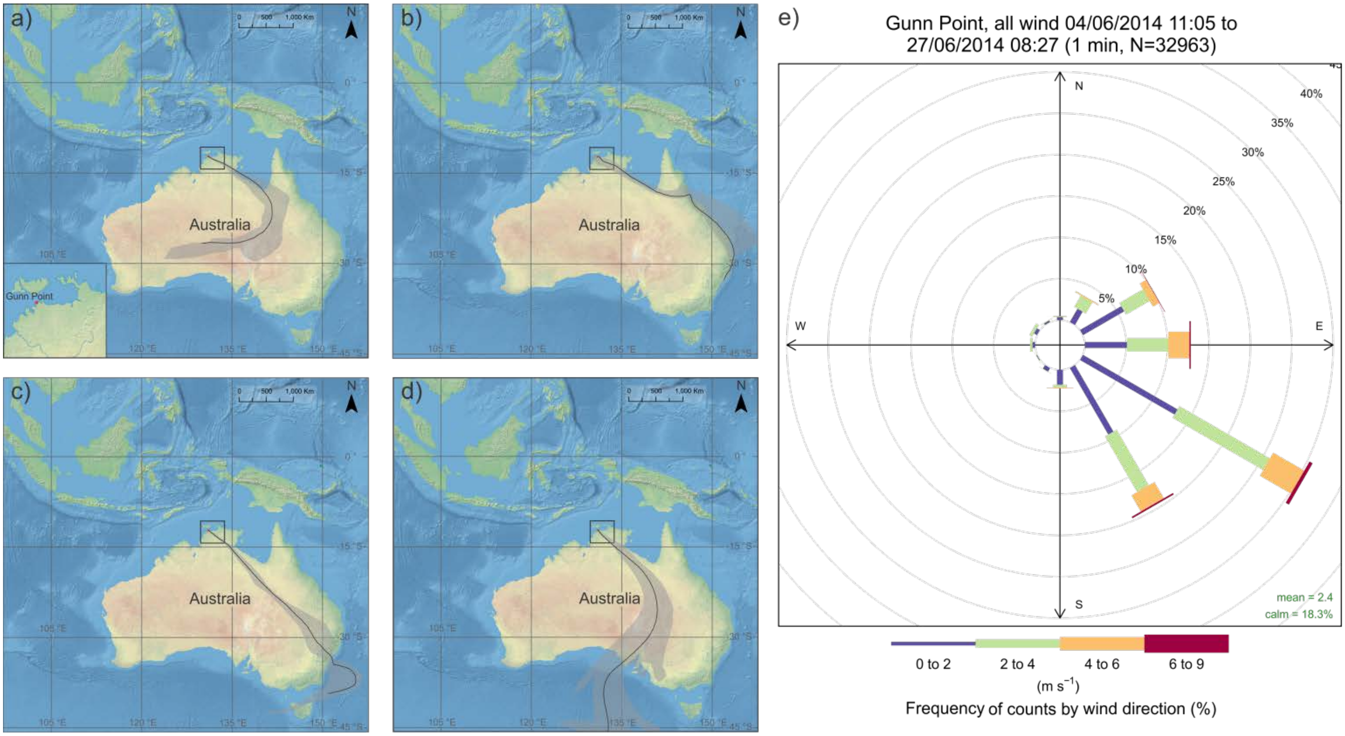


Figure 1: Location of Gunn Point study site. Insert of the Northern Territory showing the Gunn Point site and the predominant air mass fetch regions for the June 2014 Gunn Point campaign. a) Inland, low population density. b) Coastal, moderate urban/industrial activity. c) Inland, m~~M~~ajor urban/industrial activity. d) Southerly. d) Wind rose corresponding to the aerosol sampling duration. Wind rose created using the OpenAir package in R (Carslaw and Ropkins, 2012;Carslaw, 2014).

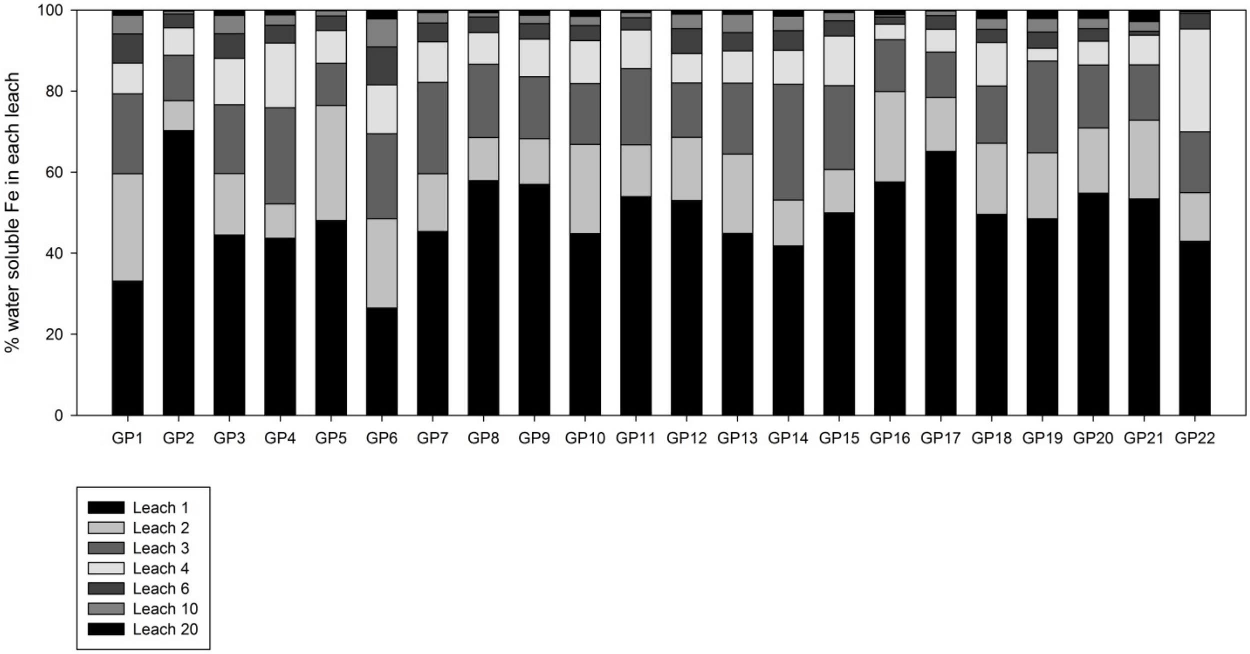
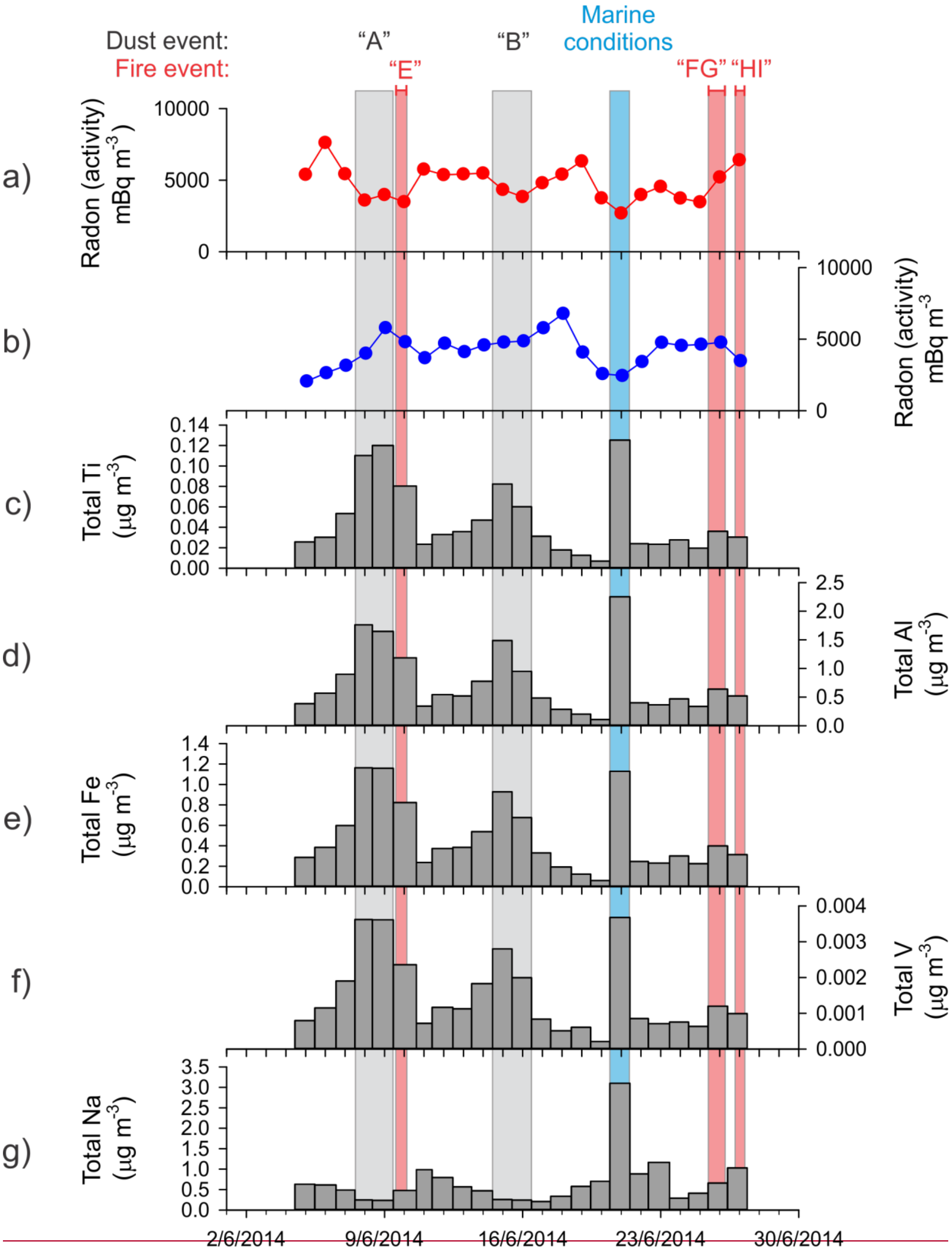


Figure 2: Fraction of water soluble iron in sequential leaches of all PM10 samples from the SAFIRED campaign. Details of samples GP1 to GP23 can be found in Table S1.


Dust event:
"A"
"B"
Marine conditions
Fire event:
"E"
"FG"
"HI"
a)
Radon (activity) mBq m^{-3})
10000
5000
0
b)
Radon (activity) mBq m^{-3}
10000
5000
0
c)
Total Ti (µg m^{-3})
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
d)
Total Al (µg m^{-3})
2.5
2.0
1.5
1.0
0.5
0.0
e)
Total Fe (µg m^{-3})
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f)
Total V (µg m^{-3})
0.004
0.003
0.002
0.001
0.000
g)
Total Na (µg m^{-3})
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2/6/2014
9/6/2014
16/6/2014
23/6/2014
30/6/2014

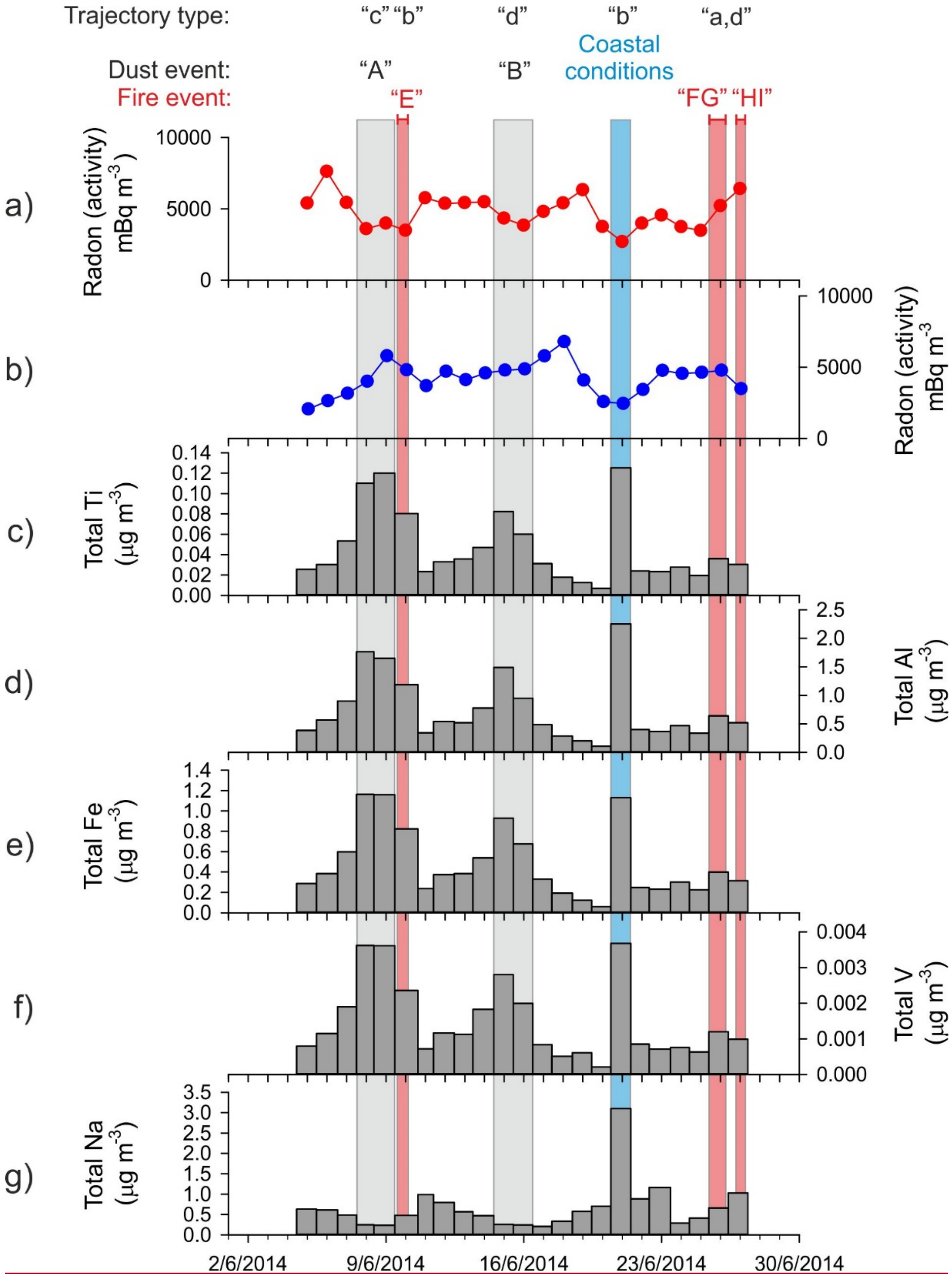
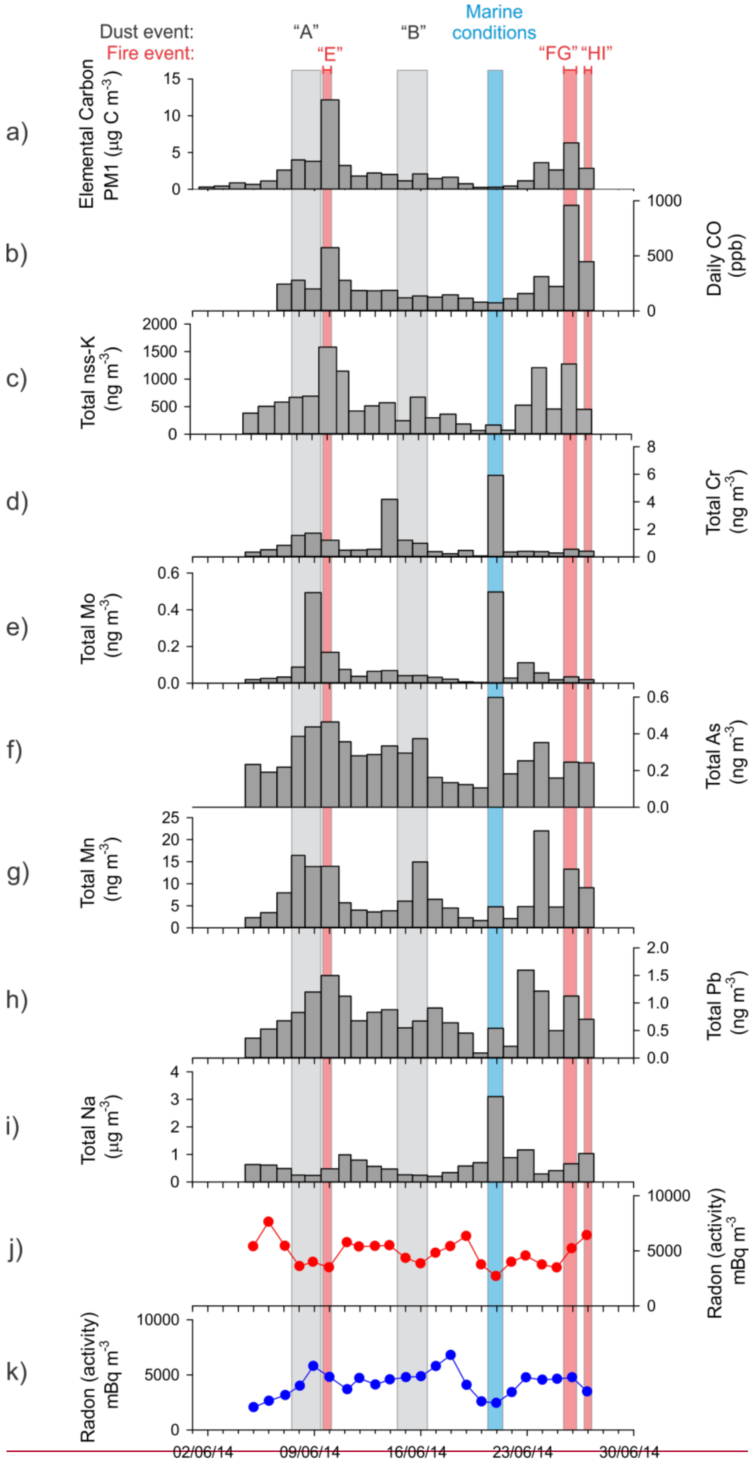


Figure 3: Time series of a) diurnal radon, b) advective radon, and total PM10 trace element concentrations c) Ti, d) Al, e) Fe, f) V, and g) Na.


Dust event:
Fire event:
"A"
"E"
"B"
Marine conditions
"FG"
"HI"
a)
Elemental Carbon PM1 (µg C m^{-3})
15
10
5
0
b)
Daily CO (ppb)
1000
500
0
c)
Total nss-K (ng m^{-3})
2000
1500
1000
500
0
d)
Total Cr (ng m^{-3})
8
6
4
2
0
e)
Total Mo (ng m^{-3})
0.6
0.4
0.2
0.0
f)
Total As (ng m^{-3})
0.6
0.4
0.2
0.0
g)
Total Mn (ng m^{-3})
25
20
15
10
5
0
h)
Total Pb (ng m^{-3})
2.0
1.5
1.0
0.5
0.0
i)
Total Na (µg m^{-3})
4
3
2
1
0
j)
Radon (activity) mBq m^{-3}
10000
5000
0
k)
Radon (activity) mBq m^{-3}
10000
5000
0
02/06/14
09/06/14
16/06/14
23/06/14
30/06/14

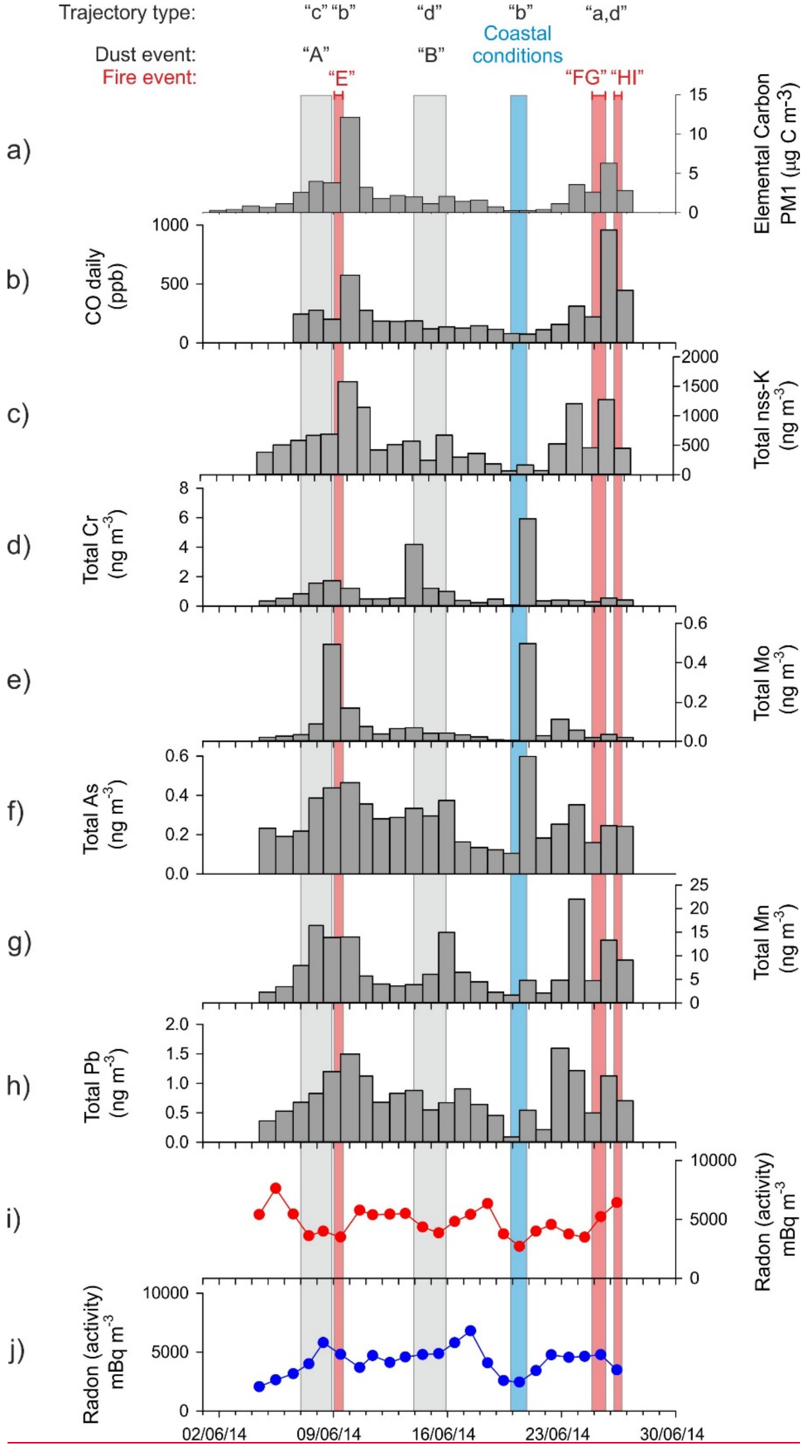
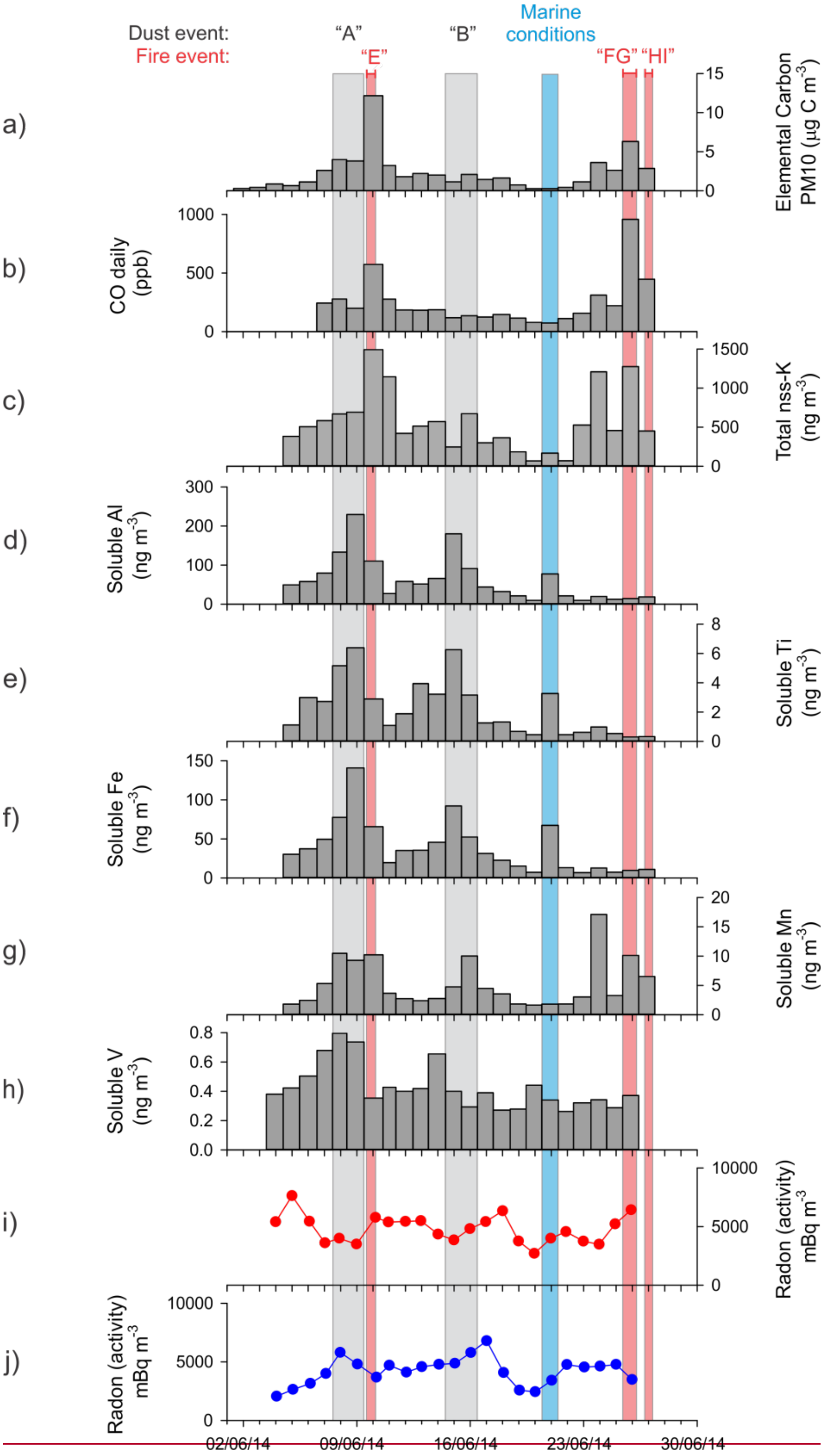


Figure 4: Time series of a) elemental carbon, b) carbon monoxide, and total PM10 trace element concentrations c) nss-K, d) Cr, e) Mo, f), As, g) Mn, h) Pb, i)~~ Na, and j)~~ diurnal radon, and j~~k~~) advective radon.



Dust event:
"A"
"B"
Marine conditions
Fire event:
"E"
"FG"
"HI"
a)
Elemental Carbon PM10 (µg C m^{-3})
0
5
10
15
b)
CO daily (ppb)
0
500
1000
c)
Total nss-K (ng m^{-3})
0
500
1000
1500
d)
Soluble Al (ng m^{-3})
0
100
200
300
e)
Soluble Ti (ng m^{-3})
0
2
4
6
8
f)
Soluble Fe (ng m^{-3})
0
50
100
150
g)
Soluble Mn (ng m^{-3})
0
5
10
15
20
h)
Soluble V (ng m^{-3})
0.0
0.2
0.4
0.6
0.8
i)
Radon (activity) mBq m^{-3}
0
5000
10000
j)
Radon (activity) mBq m^{-3}
0
5000
10000
02/06/14
09/06/14
16/06/14
23/06/14
30/06/14

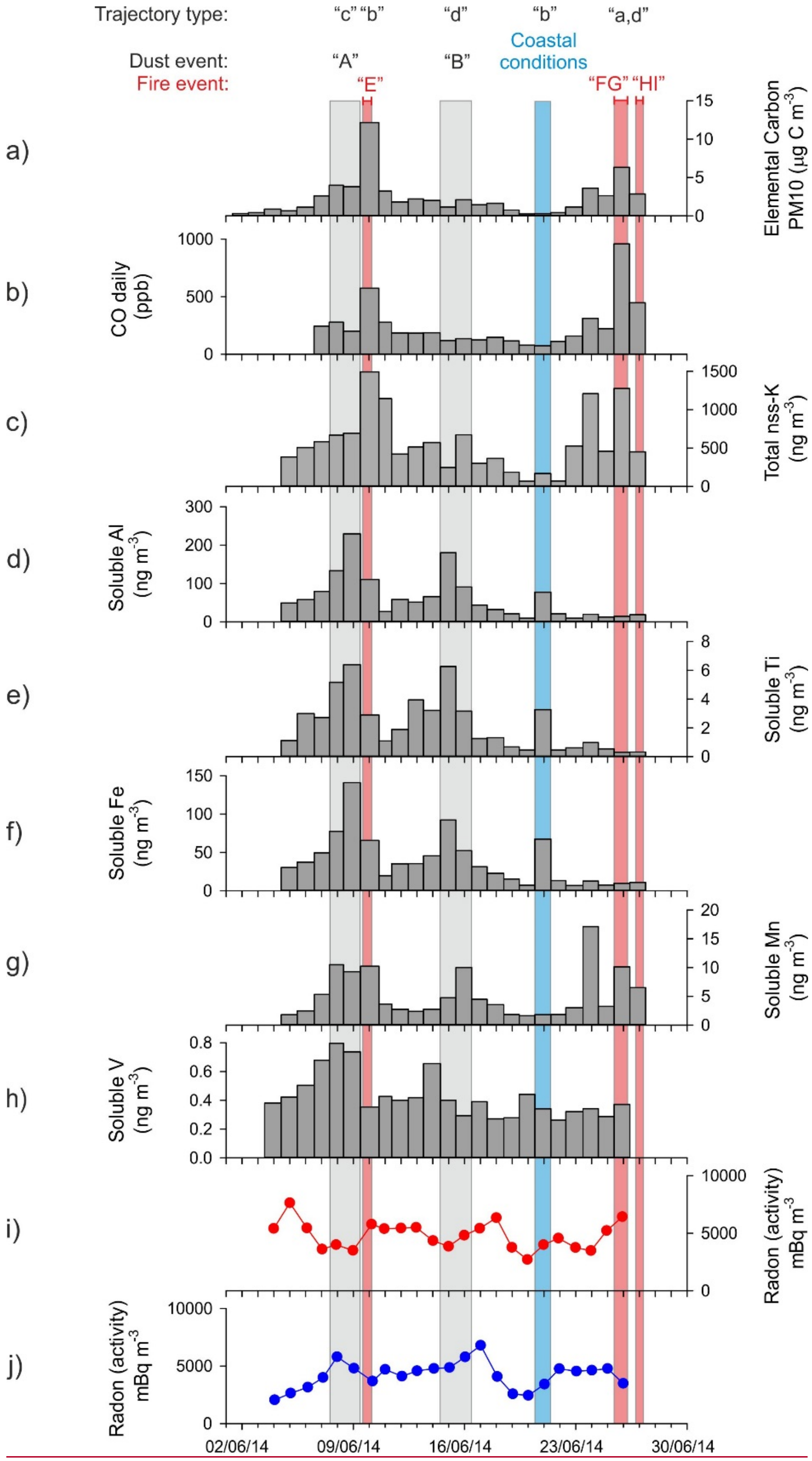
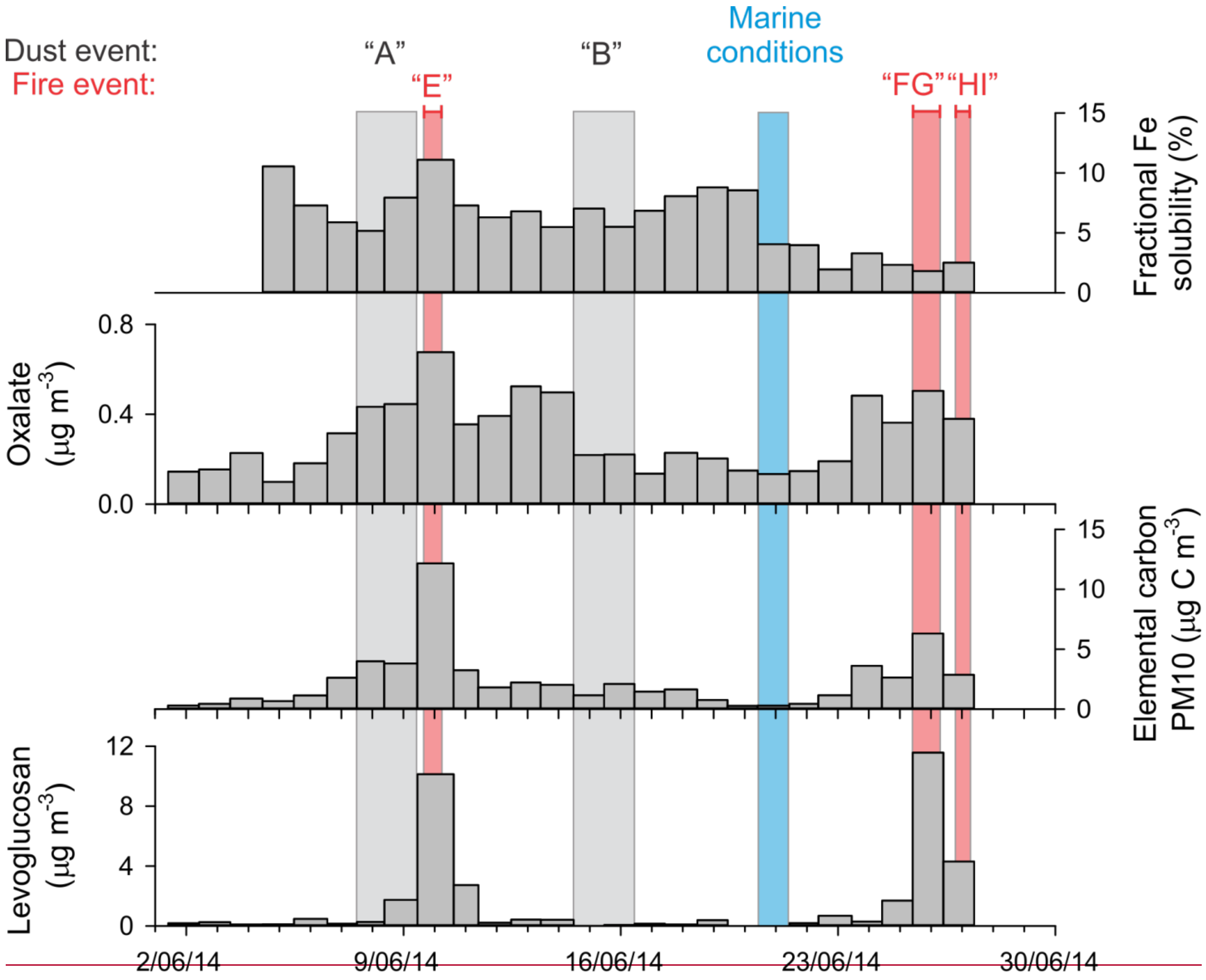


Figure 5: Time series of a) elemental carbon, b) carbon monoxide, c) total nss-K, soluble trace element concentrations, d) Al, e) Ti, f), Fe, g) Mn, h) V and i) diurnal radon, j) advective radon.


Dust event:
Fire event:
"A"
"E"
"B"
Marine conditions
"FG"
"HI"
Fractional Fe solubility (%)
15
10
5
0
Oxalate (μg m^{-3})
0.8
0.4
0.0
Elemental carbon PM10 (μg C m^{-3})
15
10
5
0
Levoglucosan (μg m^{-3})
12
8
4
0
2/06/14
9/06/14
16/06/14
23/06/14
30/06/14

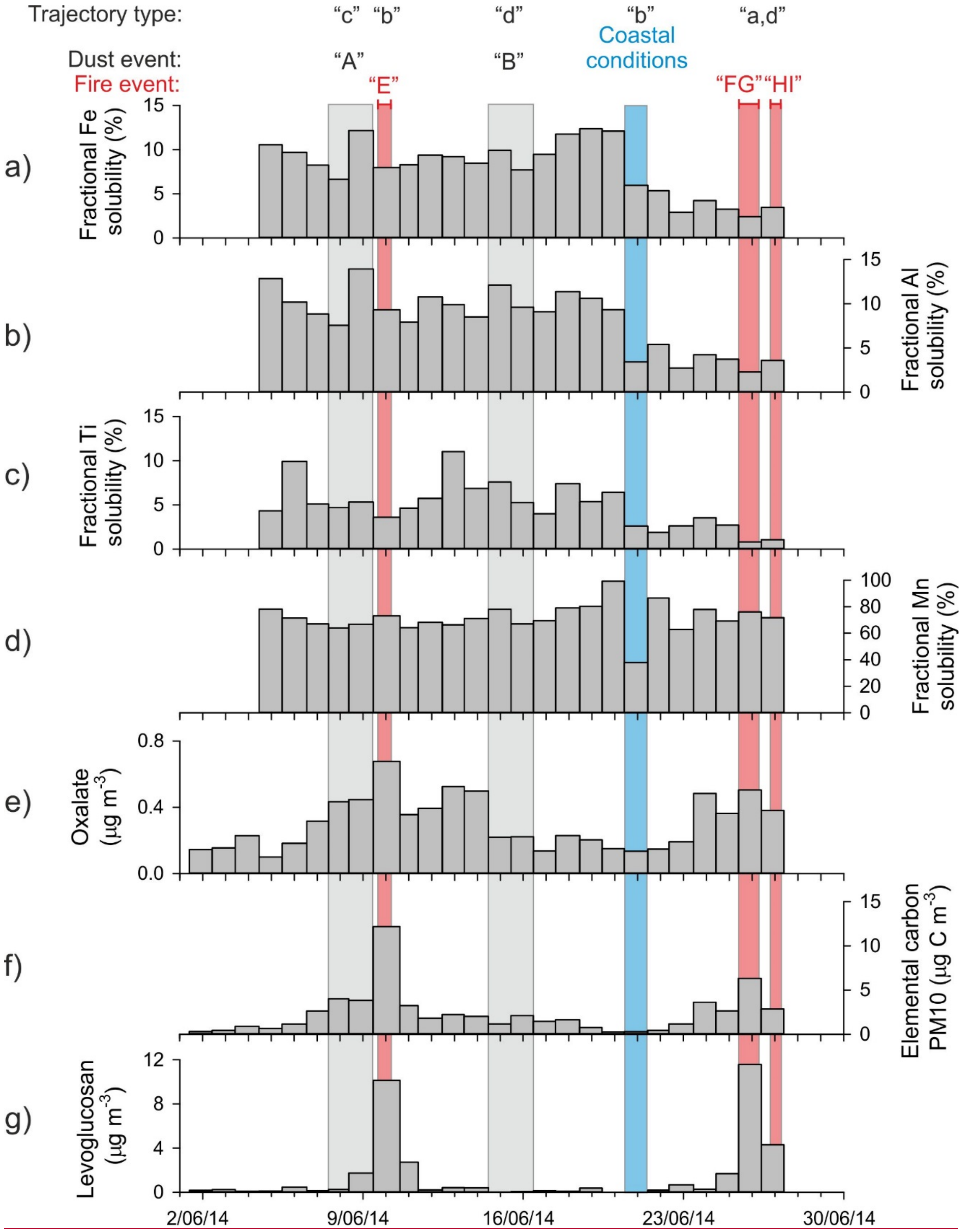
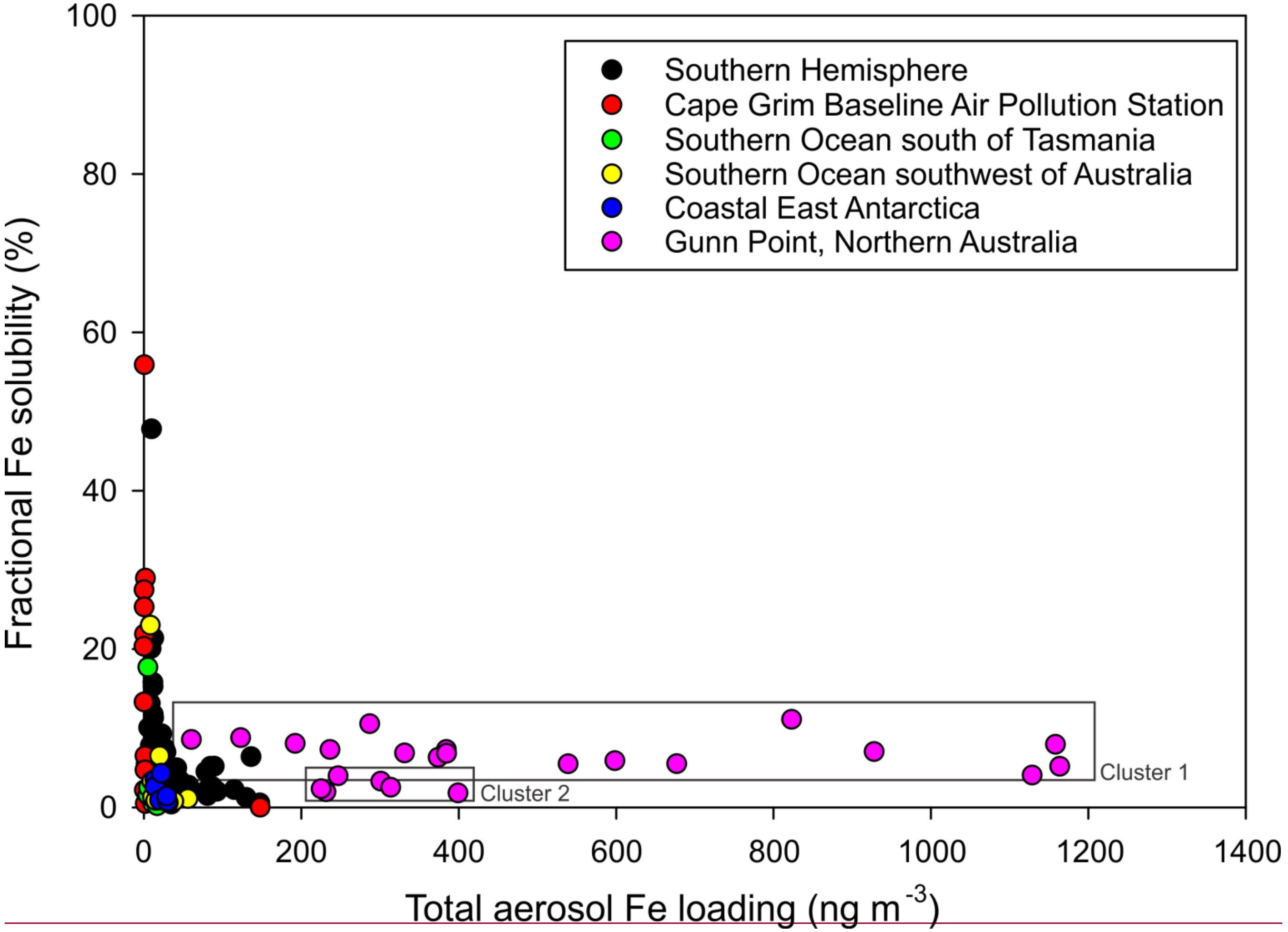


Figure 6: Time series of a) fractional Fe solubility, b) fractional Al solubility, c) fractional Ti solubility, d) fractional Mn solubility, e) oxalate, f) elemental carbon, and g) levoglucosan concentrations.


100
80
60
40
20
0
Fractional Fe solubility (%)
0
200
400
600
800
1000
1200
1400
Total aerosol Fe loading (ng m^{-3})
● Southern Hemisphere
● Cape Grim Baseline Air Pollution Station
● Southern Ocean south of Tasmania
● Southern Ocean southwest of Australia
● Coastal East Antarctica
● Gunn Point, Northern Australia
Cluster 1
Cluster 2

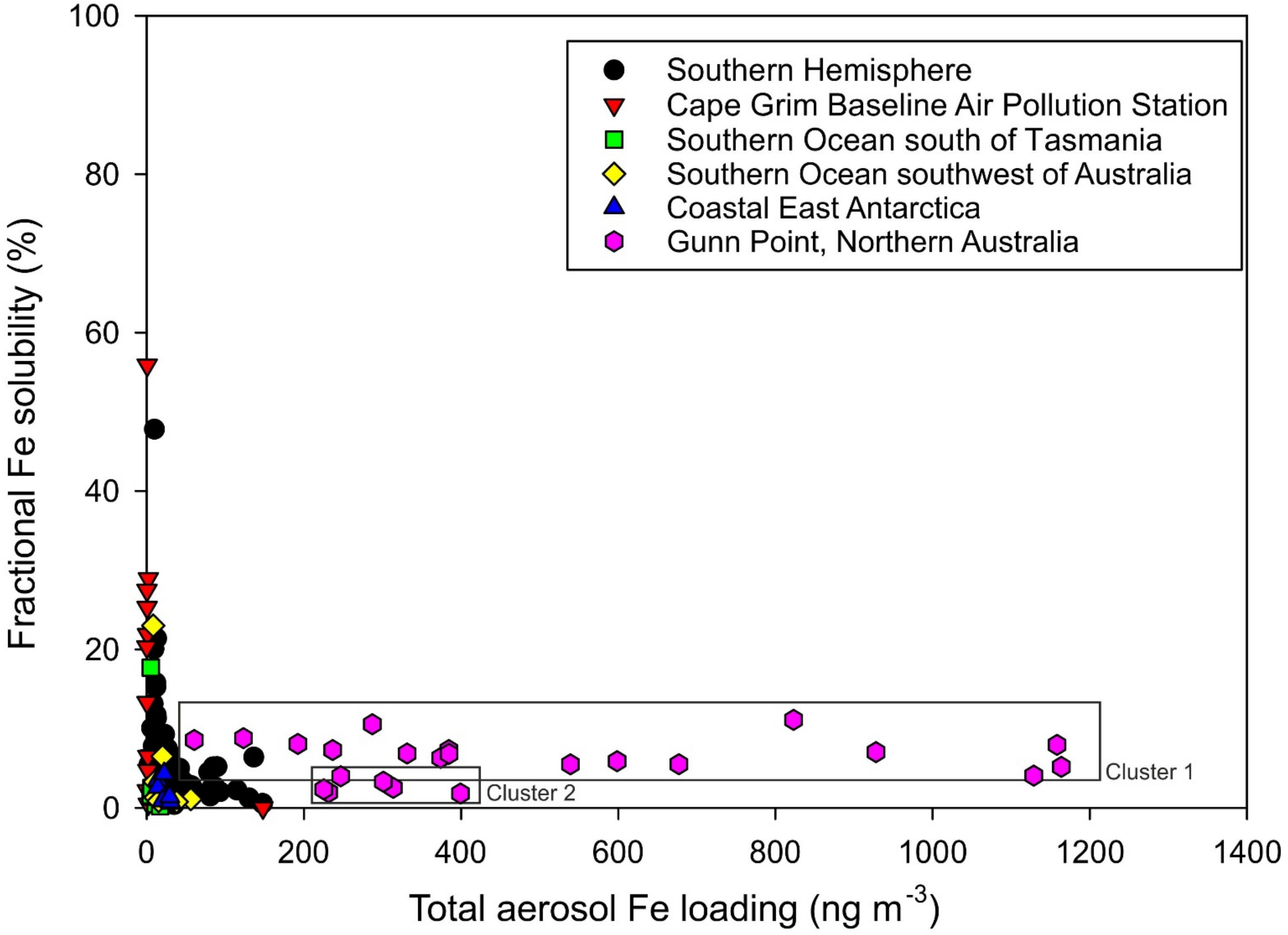


Figure 7: Gunn Point total PM10 aerosol iron mass concentration versus fractional Fe solubility superimposed on the Southern Hemispheric aerosol iron data set (Sholkovitz et al., 2012; and references within;Bowie et al., 2009;Gao et al., 2013;Winton et al., 2015). Boxes highlight the two clusters. Cluster 1: moderate fractional Fe solubility and moderate total aerosol iron loading between 5 the 4 and 19 June, and represents the upper bound of dust fractional Fe solubility for the topical dry season. Cluster 2: low fractional Fe solubility and low total aerosol iron loading between the 24 and 26 June.