Manuscript: AMT-2016-12

Author response to referee #1

We thank the referee for their time and constructive comments for improving this manuscript. We have reproduced the referee 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. Therefore they are only reproduced here if rephrasing of entire sentences was required 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

This works examines the contamination of high-volume aerosol samples during non-baseline conditions at a site well known for Southern Ocean air sampling (Cape Grim Baseline Air Pollution Station, Tasmania, Australia). Trace metal concentrations, specifically total and soluble iron, were measured and microscopy was used to show good laboratory practices for trace level iron measurements as well as contamination on a one month exposure filter. Atmospheric iron measurements in the Southern Ocean are difficult to make due to low aerosol (and iron) mass loadings and scarcity of adequate sampling locations. This paper addresses the important issue of reducing contamination when making trace metal aerosol measurements, especially in this region.

Although the implications of this work are important and it falls within the scope of AMT, the lack of data to prove the source and significance of filter contamination is problematic.

My main concerns with this paper are the number of samples analyzed (i.e. one of each kind (n=3 in tables are punches from the same filter)) and conclusions regarding the source and magnitude of contamination drawn from one month long exposure filter. One TSP and one PM10 high volume aerosol sample, collected during baseline conditions, showed suspect contamination (bugs, large mineral dust particles, etc.). The authors attributed this contamination to passive deposition during non-baseline conditions over the month long sampling periods and collected an exposure filter (filter in a sampler with the pump off) to show this (Figure 2). However, the exposure filter was collected during baseline and non-baseline conditions (as shown by HYSPLIT trajectories; Figure 7), so it is not conclusive when the contamination occurs. To accurately determine if sealing a sampler during non-baseline conditions would reduce (likely) or eliminate (not necessarily) contamination then an exposure filter should be collected during only baseline conditions or during only non-baseline conditions.

Comment: In regards to the number of samples analyzed, many blank filters were inspected by microscopy showing evidence of macroscopic material (soil, insects) similar to the examples provided in this manuscript. This evidence of contamination is not representative of the background atmosphere over the Southern Ocean. Therefore, these blanks were not analyzed by HR-ICP-MS as they did not pass quality control for baseline samples. We have added this on page 6, lines 15-18 of the revised manuscript. We agree with the referee that more one-month exposure blanks are desirable. There may be month-to month variability in the exposure blank. In an ideal world, we would have multiple high-volume aerosol samplers deployed simultaneously, some collecting blanks and some collecting samples. Unfortunately, that was not possible and at the end of the day we had to draw the line somewhere; a compromise was made in terms of cost versus benefit. In order to reduce local contamination of coarse particles, we first installed a PM10 size selective inlet on the high-volume sampler. The exposure blank was collected directly after the PM10 size selective inlet was installed to estimate contamination levels during a typical sampling period, i.e., one month. The low concentration of aerosols at Cape Grim requires month-long sampling periods to sample enough material for one soluble iron measurement. This equates to only ~12 samples per year. Therefore, we have collected one exposure blank to maximize the number of samples we can collect at the site and avoid gaps in the time series.

In order to address the magnitude of filter contamination, we have compared blank filters between the high-volume sampler deployed on the roof deck and the pneumatically sealed aerosol sampler deployed on a 70 m tower at CGBAPS (archived filter samples reported in Winton et al. (2015)). This comparison highlights that a) the aerosol iron concentrations in the archived blank filters are considerably lower than those from the high-volume aerosol sampler, and b) in comparison to the expected aerosol iron loading from archived aerosol samples, the iron blank budget associated with the high-volume aerosol sampler is large and sometimes greater than actual samples. Sealing the sampler when it is turned off, i.e., during non-baseline conditions, is therefore crucial to minimize passive deposition, local soil contamination and insects flying/crawling into the sampler. We have discussed this on page 14, lines 12-31 to page 15, lines 1-2 and provided additional data to Table 4 in the revised manuscript.

In terms of determining the source of contamination, the combination of microscope images, enrichment factor analysis, leaching experiments and local meteorology provide convincing evidence that the contamination arises from passive deposition of local soil and insects flying and crawling into the sampler. Local soil contamination in high-volume samplers on the roof deck at CGBAPS has been independently reported elsewhere (Ayers, 2001). Furthermore, observations by Cape Grim staff show that it is not uncommon for sizeable rocks to be blown onto the roof deck during extreme wind conditions (see photo 1 below). In fact, the station now has a rock collection resulting from extreme wind events. The microscope images additionally show macroscopic sized particles to up to 100 µm in dimeter in the exposure blank giving further evidence of short-range transport. It is not necessarily important whether this contamination *occurs during baseline or non-baseline conditions. We have shown that sizable physical material is delivered to the high-volume sampler which dramatically impacts the concentration of soluble and total iron concentrations in comparison to actual archived samples, and that this level of contamination does not occur in a pneumatically sealed aerosol sampler deployed up a 70 m tower. Sealing the sample during non-baseline conditions will minimize such contamination at the site as the sample filter will not be exposed to the local atmosphere during non-baseline conditions.*

The referee raises an important point, i.e., in order to accurately determine if sealing a sampler during non-baseline conditions would reduce contamination then an exposure filter could be collected during only baseline conditions or during only non-baseline conditions. This information would complete the story. However, we acknowledge that the hardware has not yet been developed to automatically collect baseline only blanks. The sampling conditions in Winton et al. (2015) cannot be replicated due to new health and safety requirements at the station that prohibit sampling and personal climbing the tower. In this respect, it is no longer possible to measure aerosol iron above the turbulent layer at Cape Grim. The data in Winton et al. (2015) represent a background soluble iron signal for which to compare the new sampling set up. Collecting a "baseline only exposure blank" or "non-baseline only exposure blank" is not practical with the current configuration of the non-sealed high-volume sampler. Collecting this type of blank would require personnel to either place a bag over the sampler or remove the exposure blank filter each time baseline conditions went in or out of sector. Furthermore, wind speed and wind direction fluctuate at CGBAPS meaning that baseline conditions can change rapidly. Contamination arising from removing and replacing the filter multiple times over a month imposes the risk of added contamination. The only way that we are aware of, to collect a "baseline only exposure blank" or "non-baseline only exposure blank" is to use a pneumatically sealed aerosol sampler (Fig. S1) such as in Bollhöfer et al. (2005); Winton et al. (2015). During baseline conditions, the trigger opens the sampler's air intake and a "baseline only exposure blank" could be collected with the pump off. The suggestion by the referee reinforces our conclusion concerning the importance of using sealed samplers in low aerosol concentration air masses.

Photo 1: Photos showing rocks blown onto the CGBAPS roof deck and the rock collection at the station. Photo credit: Jeremy Ward.

Specific Comments/Technical Corrections

Page 4 Line 1-2: ": : :a series of filter blanks and baseline aerosol samples." I find this to be a strange claim as only one of each kind of sample is reported, not a series.

Comment: By "series" we were referring to the different types of blanks collected, i.e., untreated, acid-washed, procedural and exposure. To clarify this we have rewritten the sentence on page 4, lines 1-2 in the revised manuscript:

"As the first step in developing a reliable multi-year Fe time series at the site we investigated a series of filter blank type and baseline aerosol samples."

Page 9-10 Paragraphs 1 and 2: Need citations as this is not the first study that has shown that acid washing filters is important.

Comment: We have added the following sentence, including references, on page 10, lines 13-14 in the revised manuscript:

"It has become common practice to acid-wash filters for aerosol Fe studies (e.g. Baker et al., 2006; Bollhöfer et al., 2005; Fishwick et al., 2014; Morton et al., 2013; Shelley et al., 2014; Wozniak et al., 2013)"

Page 10 Line 26: Insects could also fly or crawl into the sampler during baseline conditions.

Comment: Yes, as the sampler is not sealed insects could enter the sampler at any time. We have modified the sentence on page 11, lines 3-4 in the revised manuscript:

"Additionally, insects could fly or crawl into to sampler during baseline or non-baseline conditions, as the air inlet is not sealed (Fig. 1)."

Page 11 Line 5-7: 'This type of blank gives an indication of the relative magnitudes of the in-sector active sampling (i.e., pump turned on and controlled by the baseline switch for a month) versus passive deposition" There is no data to support this claim. This blank shows what can be passively deposited by in and out of sector baseline sampling. It is possible that during baseline conditions, especially at this height (6m), that there might be local contamination as well.

Comment: We have modified the sentence on page 11, lines 18-21 in the revised manuscript:

"This type of blank gives an indication of contamination aerosols that can be passively deposited by in and out of sector baseline sampling. The blank also givens an indication of the magnitude of local contamination during baseline conditions arising from the sampler located on a roof deck at a height of 6 m."

Page 12 Section 4.3: What would the EF be if iron was derived from long range transport? I am not sure if EF is a good way to prove this is a locally derived contamination as there are not many anthropogenic inputs in this region. Maybe some sort of principal component analysis with a larger data set would be more appropriate?

Comment: We agree with the referee that enrichment factor analysis does not discriminate the crustal signature between local and long-range transport aerosol. However, other lines of evidence clearly suggest that local soil is a major contributor to the iron budget. Such lines of evidence include; a) observations of macroscopic sized particles up to 100 µm that are too coarse to be delivered to the site via long-range transport, b) SEM imagery and EDS qualitative chemistry of individual particles which identified a range of material including carbonaceous particles, salts (NaCl, cubical crystals), mineral dust (identified by Si, Fe, Al, Ti EDS signals), silica sand, spores, gypsum, calcium carbonate, and marine aerosol (particles containing Mg, Sr and Ba), c) evidence of moths residing in the sampler (Photo 2), d) a detailed breakdown of soluble and total iron concentrations which show the majority of iron contamination is introduced to the filter during exposure (iron blank budget; Table 4), e), extreme wind speeds which deposit rocks onto the roof deck (photo 1), and f) air mass back trajectories showing that the fetch area of trajectories does not cross the Australian continent during the one-month exposure period. We have also discussed known issues of local contamination experienced in the *past with CGBAPS staff (e.g. Ayers, 2001). If we had a larger set of one-month exposure filters, principle component analysis would provide additional evidence of the source of contamination.*

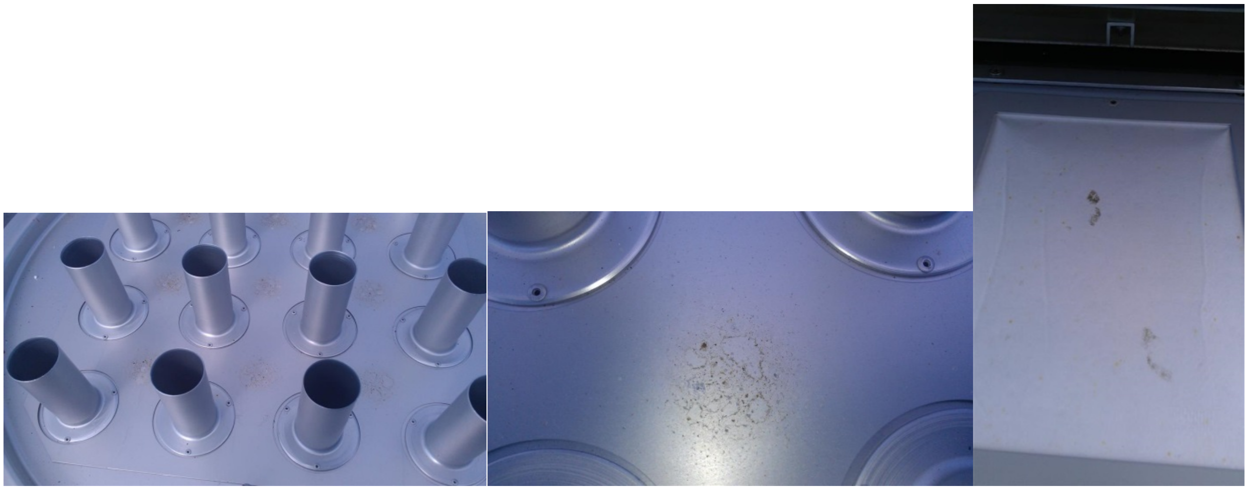

Photo 2: Photos of moth marks on high-volume aerosol sampler impactor and filter.

Page 13 Line 29-30: “The contamination was primarily due to the lack of an air-tight closure at the sampler intake.” This was not shown in this study. To show this you would need to compare a sealed and not sealed sampler at the same elevation. A direct comparison of sealing cannot be made between the 6m platform and 70m tower.

Comment: We acknowledge that the two studies are not directly comparable on page 14, lines 15-17 of the revised manuscript, however the archived samples are the only samples from the site that are not impacted by contamination. We follow the recommendation of referee #2 to put the significance of contamination into perspective by comparing the blanks reported here to real aerosol iron data from the tower. We have changed the sentence on page 14, line 30-31 in the revised manuscript:

“The contamination was is most likely primarily due to the lack of an air-tight closure at the sampler intake.”

References

Ayers, G. P.: Influence of local soil dust on composition of aerosol samples at Cape Grim Baseline Atmospheric Program (Australia) 1997-98, Baseline report 2001. 50-56, 2001.

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.

Bollhöfer, A., Rosman, K. J. R., Dick, A. L., Chisholm, W., Burton, G. R., Loss, R. D., and Zahorowski, W.: Concentration, isotopic composition, and sources of lead in Southern Ocean air during 1999/2000, measured at the Cape Grim Baseline Air Pollution Station, Tasmania, Geochimica et Cosmochimica Acta, 69, 4747-4757, 2005.

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, doi: 10.1002/2014GB004921, 2014. 2014GB004921, 2014.

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.

Shelley, R. U., Morton, P. L., and Landing, W. M.: Elemental ratios and enrichment factors in aerosols from the US-GEOTRACES North Atlantic transects, Deep Sea Research Part II: Topical Studies in Oceanography, 2014. 2014.

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, 2015.

Wozniak, A. S., Shelley, R. U., Sleighter, R. L., Abdulla, H. A. N., Morton, P. L., Landing, W. M., and Hatcher, P. G.: Relationships among aerosol water soluble organic matter, iron and aluminum in European, North African, and Marine air masses from the 2010 US GEOTRACES cruise, Marine Chemistry, 154, 24-33, 2013.