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Author response to referee #2

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. We have only reproduced the additional comments in the referee's supplement if rephrasing of entire sentences and additional data was requested. Page numbers refer to the revised version of the manuscript.

Anonymous Referee #2 interactive comment

This paper shows that "always open" hivol aerosol samplers will pick up contamination from the ambient suspended material (dust, grass, leaves, insects, insect parts, etc.), especially under windy conditions. This contamination may be great enough to contaminate real aerosol samples when the deployment conditions are not appropriate. This paper shows very detailed evaluation of the blanks associated with aerosol trace element sampling, however because no actual sample data are shown, it is not possible from this paper to judge how significant the contamination might be. I recommend adding some real data to Table 2 and 3 and 4 so put these blank values into perspective. Additional comments are inserted into the manuscript (attached file).

Comment: We agree with referee #2 that additional data from real samples is required to put the aerosol iron blank concentrations into perspective. We have compared the filter blank concentrations associated with the high-volume aerosol sampler positioned on the roof deck at the Cape Grim Baseline Air Pollution Station (CGBAPS) with actual archived aerosol samples collected using a pneumatically sealed aerosol sampler deployed on a 70 m tower at CGBAPS. This data is reported in Winton et al. (2015). The sampling conditions in Winton et al. (2015) are ideal for sampling Southern Ocean baseline air as shown by the low filter blanks in comparison to actual aerosol iron loading. However, these sampling conditions can no longer be replicated due to health and safety requirements that prohibit sampling and personnel climbing the tower.

The study reported here and the study of the archived samples use different filter substrates (Whatman 41 versus Teflon), and an additional weak acid leach was performed on the archived samples. This study also reports additional soluble and total trace element data (Al, Ti, V, Mn, Pb). We acknowledge that a breakdown of blank iron budget from these two studies is not directly comparable. Nevertheless, we have provided the "total iron blank" (from procedural and exposure Teflon filters) and the actual aerosol iron concentration data from the archived samples in Table 4 of the revised manuscript. We use the comparison between the two sampler deployments to show that contamination arising from the use of the high-volume sampler is significant.

The comparison of blanks between the two sampler deployments highlights two important points in regards to low level aerosol iron sampling in air masses over the Southern Ocean. Firstly, the aerosol iron concentrations in the archived blank filters (deployed up 70 m tower using a pneumatically sealed aerosol sampler which closes during non-baseline conditions) are considerably lower than those from the high-volume aerosol sampler (deployed on the roof deck at a height of 6 m which is always open regardless on baseline conditions). The soluble and total iron blanks of 0.0001 ng m^{-3} and 0.1 ng m^{-3} associated with the archived samples are orders of magnitude lower than the high-volume sampler blank of 0.06 ng m^{-3} and 10 ng m^{-3} respectively at the top of the tower. Secondly, 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. For soluble iron, the high-volume sampler configuration (i.e., always open and not located above the turbulent layer) could contribute between 20 - 100 % of the expected soluble aerosol iron concentration at CGBAPS. The high iron blank associated with the volume sampler of 0.06 ng m^{-3} falls within the range of archived sample concentrations of 0.01-0.3 ng m^{-3} of soluble iron. In terms of total iron, the high-volume sampler blank of 10 ng m^{-3} is significantly greater than actual aerosol concentrations at the site that range between 0.04-5.8 ng m^{-3}. Given the low level aerosol iron loading over the Southern Ocean, these blanks are considerable and, at times, could completely overwrite the true aerosol iron signal in baseline air. Sealing the sampler 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.

Response to supplementary comments

Page 2, line 25: Estimates of what?

Comment: "soluble Fe" has been inserted.

Page 4, lines 20-25: Sentence is much too long. Break it up and make sure it makes sense grammatically.

Comment: Sentence has been rewritten:

"In order to extend the short aerosol Fe time series of Winton et al. (2015), we have established a Fe aerosol monitoring program at CGBAPS. We followed the GEOTRACES sampling and handling protocols for trace metal analysis (Cutter et al., 2010; Morton et al., 2013). In addition, we followed the United States Environmental Protection Agency (EPA) standard, described by (Chow, 1995), for the sampling of ambient air for total suspended particulates (TSP; all particle

sizes) and PM10 (particulate matter diameter <10 μm) using a high-volume aerosol sampler. The EPA standard covers the sampler instalment, calibration and operating procedure."

Page 11, lines 1-2: You do not present any aerosol Al data for Southern Ocean baseline air, and in fact do not present any actual data from actual samples, so how can one judge whether the Al filter blank might be a problem?

Comment: We agree that actual Al data is required to provide an assessment of whether Whatman 41 filters are suitable for aerosol Al studies in baseline air. The sentence has been rewritten and we have deleted the sentence concerning the suitability of Whatman filters for Al studies in the conclusion on page 16, line 1.

"Our soluble Al blank concentrations were also greater for the acid-washed filter highlighting the need for a systematic study of blank aerosol filters in baseline air. The Whatman 41 filters are only suitable for trace metal aerosol studies when the sample concentration is above the detection limit. Aerosol Al concentrations have been reliably reported in regions where the aerosol loading is considerably greater than the Southern Ocean. However, if the sample concentration is too low in baseline air, then we recommend that the sampling time is increased to collect a higher concentration of trace metal aerosols on the filter."

Page 14, lines 1-2: This "loading" estimate is not given. Please provide data showing the actual sample concentrations.

Comment: We use the comparison of blank filters between the high-volume sampler deployment and the pneumatically sealed aerosol sampler deployed on a 70 m tower at CGBAPS (Winton et al., 2015) to show that contamination arising from the use of the high-volume sampler is significant. We have added additional data to Table 4 and discussed this on page 14, lines 12-31 to page 15, lines 1-2 as per our response to the interactive comment above.

Table 2: Table column format seems messed up. I assume this gets fixed during publication? Which row is for the Savillex Beaker blank (the labeling is not consistent).

Comment: Column format has been corrected. The Savillex Beaker blank is the digestion blank. We have clarified this terminology in the caption of the table.

Table 2: Where is the DL value actually provided? I see <0.001 in the instrumental blank row for Mn. Is that the DL?

Comment: We have added the detection limit in the first row of the table.

Table 2: These numbers do not match those used in Table 4 for Fe.

Comment: The blank iron budget was constructed using the series of different blank filter types, but not each blank necessarily relates to an item in the blank budget. For example, to determine the contribution of iron to the budget from the acid washed filter substrate, the concentration of total iron from the digestion, instrument and acid-washed filter blank was subtracted from the total iron concentration of the untreated filter. Please see notes in the footer for how the blank iron budget was constructed.

Table 3: Same comments as fro Table 2. DL not defined and values not given?

Comment: We have added the detection limit in the first row of the table. DL is now defined in the table caption.

Table 4: Please compare these results to the actual data from a real deployment when the tower was being used. It is not clear whether these blanks are dramatically higher than actual concentrations.

Comment: Data from Winton et al. (2015) has been added to Table 4.

References

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.