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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temporally-Delineated Sources of Major Chemical Species in High Arctic Snow" *by* Katrina M. Macdonald et al.

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Temporally-Delineated Sources of Major Chemical Species in High Arctic Snow – Response to Anonymous Referee #3

Referee comments received and published: 23 October 2017 (quoted below)

We would like to thank Referee #3 for providing comments on this manuscript. We greatly appreciate the care with which the three referees have reviewed this manuscript and the improvements gained through their insight.

Response to Referee Discussion

Referee Comment: Review for Atom. Chem. Phys. Discuss. Temporally-Delineated

Source of Major Chemical Species in High Arctic Snow General review: The paper provides apportionment of chemical components in high Arctic snow, which is of interest. Some of the interpretation of source region and emission source connected to the PMF factors was not sufficiently supported and seemed stretched; this was particularly true for the discussion for the sulfate factor and the attribution of V, As and Se to dust/crustal materials in the dust factor. Improved consistency is needed for naming across the text, figures, and tables. I agree with comments provided by the previous referees. Response: We agree that factor naming should be consistent throughout. The revised manuscript uses the following names when referring to factors 1 to 7, respectively: sea salt, crustal metals, black carbon, carboxylic acids, nitrate, non-crustal metals, and sulphate. Please see the responses to referee #1 and #2 for specific replies to their comments. âĂČ Response to Detailed Comments

Referenced to Page/Line #(s) in the original manuscript:

3/5-7

Referee Comment: You need to give a bit more detail here, regardless of whether you are following previous protocol as this paper needs to be able to stand alone. How are these melted? How is the filtration accomplished? What is the storage protocol? How are the blanks?

Response: Additional details on the sample preparation and analysis have been provided in the revised supplemental, section S1.

6/17

Referee Comment: Please make this more explicit, especially for ones where the is temporal overlap in the peak concentration of the factor.

Original Line: The potential FLEXPART source regions associated with each PMF factor were identified.

Response: The calculation of the weighted FLEXPART source/influence regions is

described in Equation 4. (revised manuscript page/line(s): 6/4) In response to the existence of temporal overlap, we found that no two factors share more than two dates with peak above their respective 90% percentile. The text has been revised to note this (6/15-16). The highest correlation in factor contribution over time was seen between Factor 3 black carbon, Factor 5 nitrate, and Factor 6 non-crustal metals, with Pearson's correlation coefficient of 0.38 to 0.52. No other factors exhibited contribution correlation coefficients greater than 0.3. Furthermore, factors with similar peak periods may suggest similar source regions; thus the resultant similarities in the FLEXPART plots is not unexpected.

8/12

Referee Comment: Please make all factor names consistent: sea salt/marine sea salt/marine factor, choose one and use for all tables, text and figures.

Response: As per the response above, all references to the factors by name have been revised to be consistent.

9/13

Referee Comment: You should be able to find the ice extent for these specific time periods for the locations mentioned. Also, based on the heat map in Figure 3 for Factor 1 (you should really include the Factor names here as well, as it is difficult to keep track of which factor is which across a couple figures), the longest residential time is north of Greenland and Siberia – are these areas open water in January 2015? Wouldn't the open water have to have been close to the site for the correlation to local wind speed be relevant for sea spray sourcing?

Response: Per the referee's suggestion, sea ice concentration plots have been obtained from the NOAA G02135 archives (ftp://sidads.colorado.edu/DATASETS/NOAA/G02135/). Comparison of these plots and the potential source regions identified for Factor 1, sea salt, showed several

potential sources for sea salt: Barents Sea, Greenland Sea, Norwegian Sea, northern Atlantic, and portions of Baffin Bay and waters surrounding the Queen Elizabeth Islands. This information has been added to the manuscript (12/9-12).

Factor names have been added to Figure 3 (revised page 10).

The correlation between Factor 1, sea salt, and local wind speeds was weak, a Pearson's correlation of 0.28. We agree that for local wind speeds to be relevant there must be a local source of sea salt. This could include any local open water, blowing saline snow, or frost flowers; however, we would require more data to confirm the existence of any of these sources at the specified time. Upon further consideration, we have noted that Factor 1, sea salt, in fact has a stronger correlation with collection period length (Pearson's correlation coefficient of 0.47). The January peak of this factor was one of the longer collection period of the campaign. This may suggest that the deposition of sea salt aerosol was relatively continuous over time; thus longer collection periods were associated with higher sea salt signatures. However, it should be noted that both of these correlations are fairly weak (the 0.28 correlation has been deemed too weak to include in the revised manuscript), so these inferences should be considered uncertain. Section 3.2.1 of the manuscript has been revised to reflect the discussion above.

Figure 1

Referee Comment: Clarify whether these are soluble, insoluble or total metals.

Response: As stated in Section 3.1, only the portions of the ICP-MS metals considered insoluble were included in the PMF analysis. The caption for Figure 1 has been revised to restate this information.

11/3

Referee Comment: Make all factor names consistent throughout the manuscript: crustal metals vs dust. Also, the high contribution of V, As and Se might indicate anthropogenic pollution (i.e. coal or heavy oil combustion) not just "dust".

Response: Per comment above, factor names have been revised to be consistent throughout the text.

We agree that V, As, and Se are all typically thought of as anthropogenic in origin; yet, they all also exist in soils. This comment was addressed in response to Referee#1, copied below: While we agree that V, Se, and As are typical of anthropogenic sources they also occur in dust sources. The ratio of these metals to Al in Factor 2, crustal metals, were 0.0016, 0.0031, and 0.00081 m/m for V, Se, and As, respectively. Soils vary significantly in composition, but typical ratios to Al are 0.0012 - 0.0016, 0.000001 - 0.00027, and 0.00002 m/m for V, Se, and As, respectively (Taylor, 1964; Barrie, den Hartog, and Bottenheim, 1989; Masson-Delmotte et al., 2013). Measurements of local crustal sources in the Arctic have also seen ratios to Al of 0.0013 and 0.00013 m/m for V and As, respectively (Se not measured) (Barrie, den Hartog, and Bottenheim, 1989). As discussed in the manuscript, this gives enhancement ratios of approximately unity for V, 11-5000 for Se (note this large range is a result of the high variability in crustal measurements), and 6-37 for As. Thus, the loading of V in particular on this factor is very reasonable for a crustal source. The loadings of Se and As are higher than for typical soils but given the variability seen across crustal sources both could still be explained by a crustal source. Furthermore, the raw unapportioned concentration measurements of V, Se, and As all correlate to Al with Pearson's correlation coefficients of 0.91 or higher. Timeseries of these analytes are provided in the supplemental.

An important distinction in this analysis is that the V, Se, and As measurements being discussed are the insoluble portions (as noted in the original manuscript page 7 lines 31-32, and revised manuscript page 6 lines 2-3). The soluble portion of these metals was often below detection limits with weak signal-to-noise and therefore was excluded from the apportionment analysis (note that the portion considered as "soluble" would include soluble metals as well as insoluble metals associated with particles capable of passing through a 0.45 μm filter; Macdonald et al., 2017 provides further details about this analysis). Of these three metals soluble As had the highest number of measure-

ments about detection limit. The soluble As time series correlated best with Factors 3 and 6, black carbon and non-crustal metals. The limited data available for soluble metals contributes a high degree of uncertainty to any discussion of their potential apportionment, but their correlation with these anthropogenic factors may indicate that the anthropogenic sources of these metals were mostly captured in the soluble measurements while the insoluble measurements represent a largely crustal source.

Figure 3

Referee Comment: The cyan diamonds and green triangles are very difficult to see.

Response: We agree that the symbols denoting Alert and volcanic sources are quite small (as noted by both referee #1 and 3). This was done so as to not block a significant portion of the trajectory plot. This figure will be uploaded as a high-resolution image allowing readers with difficulty seeing these symbols to simply zoom in as needed, without sacrificing the details of the trajectory plot.

14/10

Referee Comment: For Russian BC sources, there have been two new studies in the last year that should be included here and incorporated into the discussion:

Evans, Meredydd, Nazar Kholod, Teresa Kuklinski, Artur Denysenko, Steven J. Smith, Aaron Staniszewski, Wei Min Hao, Liang Liu, and Tami C. Bond. "Black carbon emissions in Russia: A critical review." Atmospheric Environment (2017).

Winiger, Patrik, August Andersson, Sabine Eckhardt, Andreas Stohl, Igor P. Semiletov, Oleg V. Dudarev, Alexander Charkin et al. "Siberian Arctic black carbon sources constrained by model and observation." Proceedings of the National Academy of Sciences (2017): 201613401.

Response: We thank the referee for the suggested references.

Evans et al. (2017) reviews a body of work related to BC sources within Russia. This

study develops a comprehensive budget of Russian BC emissions. Specifically, flaring and transportation are noted as major sources. Reference to the work by Evans et al. (2017) has been added to the manuscript. (14/33)

Winiger et al. (2017) is a study of the sources of BC to the Siberian Arctic from based on aerosol and isotope observations at Tiksi and comparison with dispersion modelling results. This paper highlighted the Autonomous Okrugs of Khanty-Mansi and Yamalo-Nenets regions as a hotspot for BC emissions, particularly in the winter months. This aligns with the regions of Russia noted as potential sources to Factor 3, black carbon, as shown in Figure 3 of the manuscript. Winiger et al also identified domestic and transportation activities as the major sources of BC to the Siberian Arctic (35% and 38%, respectively), with lower contributions from flaring, power plants, and open fires (6%, 9%, and 12%, respectively). Reference to the work by Winiger et al. (2017) has been added to the manuscript. (15/1)

Page 14

Referee Comment: For detailed comparison with previous high Arctic snow apportionment studies, do also take into account more of the potential impact of Arctic location. The Hegg studies were quite different in the study design, representing PMF of a large number of Arctic sites as opposed to PMF at a single Arctic site.

Response: The difference in these studies is noted in Table 2 in the original document which lists the current study as temporally-refined and the Hegg studies as spatially-refined. However, per the suggestion of the referees, Table 2 has been removed from the revised text. The significance of location to BC source make-up has been noted in the revised text. (12/9-12 and 12/23-25)

Table 2

Referee Comment: Include location of the studies. The location is very relevant in terms of understanding BB impact across the Arctic. For the apportionment/co-

variance (again, use the same terms in the text and tables to avoid confusion), include types of species used in the modeling for BC apportionment.

Response: This table, Table 2 in the original manuscript, has been removed from the revised manuscript per the referees' suggestion.

Page 16

Referee Comment: I think this sentence has been truncated "...linked with both biomass burning plumes..." and?

Original Line: Carboxylic acids within the Arctic have previously been linked with both biomass burning plumes (e.g., Jaffrezo et al., 1998; Legrand and de Angelis, 1996).
Response: As also noted by referee #1 the word "both" in this sentence was a mistake. The sentence has been corrected to remove the word "both". (15/20-21)

17/13

Referee Comment: Where are source areas shown in Figure 2?

Response: The referee is correct that this line mistakenly referenced Figure 2 instead of Figure 3. This has been corrected in the revised manuscript. (15/3)

17/15-16

Referee Comment: It's not clear how this factor coincides with increased transport over the ice-free Norwegian Sea and northern Atlantic. Remove unless you can support.

Response: This section has been revised as follows to provide greater clarity: "Weighting the FLEXPART predicted source areas by the Factor 1 peak dates (Figure 3) showed the Eurasian coast of the Arctic Ocean, the Norwegian Sea, the Greenland Sea, and the northern Atlantic Ocean to be potential sources of sea salt to Alert. Ice-free areas were identified using the NOAA G02135 ice concentration images (retrieved from ftp://sidads.colorado.edu/DATASETS/NOAA/G02135/ November 2017). During periods of peak Factor 1, sea salt, contribution, the East Siberian Sea, Laptev Sea

and Kara Sea appear to have been largely ice-covered; however, the Barents Sea, Greenland Sea, Norwegian Sea, northern Atlantic, and portions of Baffin Bay and waters surrounding the Queen Elizabeth Islands all seem to have been ice-free or with new, thin ice coverage. Thus, sea salt spray from these areas likely contributed to the sea salt signal at Alert.". (12/9-16)

18/20-21

Referee Comment: The Flexpart in Figure 3 does not seem to match with the assignation of sulfate to volcanoes and the Smoking Hills.

Response: The Factor 7, Sulphate, section has been revised to address several comments from all referees. We recognize that Figure 3 does not show high influence from the noted volcanic sources for Factor 7; however, this plot only represents a ten-day back trajectory and does seem to indicate that Factor 7 is more likely a dominated by relatively local sources rather than long-range anthropogenic sources. Furthermore, these plots only highlight areas over which the trajectories passed within 500 m of the surface (as noted in section 2.4.2). This approach is useful for identifying ground-level sources which could have reasonably impacted the air mass. However, volcanic sources can impact air masses to a much great height, given the heat and velocity of the emitted plume; thus, trajectories at a greater height should be considered. We have reviewed the FLEXPART influence plot for Factor 7 for trajectories within 10 km of the surface and this plot does show greater potential influence from the BárÃřarbunga volcano in Iceland and the Smoking Hills in Canada. (section 3.2.7)

Page 18-19

Referee Comment: The explanation for the sulfate factor was a bit forced to match volcanism. If the metals factor was combined with sulfate in the six factor solution, it would seem that would indicate an anthropogenic source. When comparing to the connected Macdonald paper, the co-variance of sulfate and MSA (or MS, as it was called in the previous paper), might be spurious as MSA is only high in the early part

of the campaign.

Response: The six-factor solution produced a factor which roughly combined Factors 6 and 7 of the seven-factor solution; however, it does not reflect the observed seasonal trend in sulfate. The distinct fall peak in sulfate observed in this study is not predicted by the six-factor solution and as a result the sulfate predicted/measured fit is very poor (Pearson's correlation coefficient of only 0.38). The addition of the seventh factor enabled better recreation of the observed sulfate signal. The revised manuscript has been updated to include mention of this in the manuscript (19/7-10) and supplemental (Section S3.2 ad Figure S7).

Figure 4

Referee Comment: use the same naming for factors across all figures, text and tables. The abbreviation is difficult here.

Response: Figure 4 has been revised to use the full names for each factor.

21/13

Referee Comment: again, take location into account for comparison with other Arctic BC studies.

Response: Per the suggestion of the referees, the conclusions have been revised to reduce the focus on BC. The discussion of BC results has been changed to stress the importance of spatial and temporal variation in the BC sources.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-718/acp-2017-718-AC3-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-718, 2017.