Temporally-Delineated Sources of Major Chemical Species in High Arctic Snow – Response to Anonymous Referee #1

Referee comments received and published: 7 September 2017 (quoted below in blue text)

We would like to thank Referee #1 for their detailed comments and discussion. We greatly appreciate the care with which the referee has reviewed this manuscript and the improvements gained through their insight.

Response to Referee Discussion

Referee Comment: This manuscript is the second to report on the results of 9-10 month long campaign (September to June) characterizing the chemical composition of fresh snow sampled at Alert. The first paper presented the data and compared it to simultaneous measurements of aerosol composition to assess the efficiency of air to snow deposition for the different analytes. Here the focus is application of PMF and the FLEXPART transport modeling tool to assess source regions for the various chemical compounds measured in the snow.

This is a solid piece of work, though I feel that the manuscript is less accessible than it could be (more on that below). I also suggest that the authors should consider changing the emphasis in several places in the discussion, to better reflect a lot of other recent (and also pioneering) work on related topics. A very good example of this arises as early as the abstract, where the finding that BC in the high Arctic during winter is dominantly from anthropogenic sources (fossil fuel combustion) and not biomass burning is highlighted. In section 3.2.2 their analysis refines this even more and points to sources in Eurasia for nearly all of this anthropogenic BC. To me, this is basically rediscovering some of the very early findings from a host of “Arctic Haze” investigations initiated in the 1970s which documented that the Haze was largely pollution, it was significantly absorbing due to BC, and much of it came from relatively high latitudes in Europe and Russia. Authors note that their work is focused on snow rather than aerosol, yet they explicitly assert that the snow is providing constraint on aerosol sources, so this “finding” is reassuring but perhaps not so exciting as to merit being the only factor from the PMF to be called out in the abstract. This statement about BC in the abstract notes that it is a “light-absorbing compound critical to the Arctic radiative balance” which is certainly true. However, the AMAP, 2015 assessment (cited frequently in this manuscript) points out that a suite of CTMs all agree that Asian sources dominate the atmospheric burden and climatic impact of BC in the Arctic. Most likely this apparent discrepancy is due to the highly stratified Arctic winter time troposphere, allowing Eurasian BC sources to be dominant in lower levels (sampled at surface aerosol sites and scavenged by mid- to low-level clouds) while Asian BC is at higher altitudes. In any case, I find the present result that essentially no Asian BC gets to Alert within 10 days more interesting than seeing very little biomass burning smoke in the high Arctic during winter.

Response: We thank the referee for their time in commenting on this manuscript.

We agree that there is existing evidence pointing to a significant anthropogenic influence on particle black carbon (BC) levels in the Arctic. However, we would like to note that some recent studies specifically of the sources of BC in Arctic snow samples (i.e., Hegg et al., 2009; Hegg et al. 2010) have suggested that biomass burning is the dominant source of BC found in Arctic snow. Furthermore, as per the comment of referee #2, it has been suggested that the dominant source of BC to Arctic snow may vary by location or time of year. Thus, we think that additional evidence on the sources of BC to Arctic, specifically the portion that is deposited to Arctic snow, is important to discuss.

We do agree that the manuscript would benefit by expanding the focus beyond BC. Several revisions have been made to the manuscript to give more attention to other chemical species critical to the Arctic atmosphere, as suggested above and in following referee comments. We have also added discussion on the geographic source of BC, with the findings of this paper indicating a largely central Eurasian source as opposed to an East Asian source. We would like to thank the referee for this suggestion.

Referee Comment: A very interesting finding in this work is the lack of a strong anthropogenic sulfate signal. Arctic Haze "comprises a varying mixture of sulfate and particulate matter and, to a lesser extent, ammonium, nitrate, dust, and black carbon (e.g., Li and Barrie, 1993; Quinn et al., 2002)" (Quote from chapter 4 of AMAP, 2006; another work cited several times in this manuscript. This statement is also repeated nearly verbatim on page 2 lines 10-11 of this manuscript.) This may reflect imperfect air-snow transfer of a defining characteristic of the Arctic winter-time troposphere, greatly enhanced sulfate, or possibly strong impact from volcanic sources in this particular year (suggested by the authors, but not very convincingly). Critically assessing air to snow transfer of sulfate would provide a nice link to the first paper in this series. However, the missing Arctic Haze sulfate signal could also reflect problems arising from sampling fresh snow from elevated snow tables (see more on this in first detailed comment below).

Response: We agree with the referee that the apportionment of sulphate in this study is interesting. While the majority of sulphate is apportioned to Factor 7, sulphate, a significant mass, 24 µg/m^2/period, is also apportioned to Factor 3, BC. Compared to the mass apportionment of BC to Factor 3, 1.4 µg/m^2/period, this gives a ratio of about 17 mass/mass SO_4^{2-}/BC. This appears to be similar to the ratio typically observed in Arctic Haze of 10-20 mass/mass (e.g., Hopper, Worthy, Barrie, and Trivett, 1994; Sharma, Lavoué, Chachier, Barrie, and Gong, 2004; Gong et al., 2010 to name a few). Thus, the SO_4^{2-} apportioned to Factor 3, BC, seems appropriate for Arctic Haze. Furthermore, SO_4^{2-} was observed to have significant mass loading of 46 µg/m^2/period on Factor 6, non-crustal metals, also considered to be anthropogenic in origin.

As the referee noted, the previous publication Macdonald et al. (2017) found SO_4^{2-} to show a higher deposition velocity than BC, especially in the warmer fall months. Several factors likely contributed to this trend. A potential explanation could be that heightened SO_2 scavenging in the fall lead to an increased level in the snow relative to BC. Specifically sulfate/SO_2 from volcanic sources prevalent in the fall may have been scavenged more readily than BC, resulting in an enhanced SO_4^{2-} deposition velocity and the identification of a separate SO_4^{2-} dominated factor in the fall. Additional research would be required to confirm this hypothesis (i.e. the SO_2 would have to be oxidized to sulfate in the precipitation or snow), but we believe it is a reasonable explanation of the observations of these two papers. The discussion of Factor 7 has been revised to expand on these points and we would like to thank the referee for their suggestion.

Please see the response to the first detailed comment for a discussion on the impact of undercatch on the sulphate signal.

Gong, S. L., Zhao, T. L., Sharma, S., Toom-Sauntry, D., Lavoué, D., Zhang, X. B., Leaitch, W. R., and Barrie, L. A.: Identification of trends and interannual variability of sulfate and black carbon in the Canadian High Arctic: 1981-2007, J. Geophys. Res.-Atmos., 115 (D07305), 1–9, doi:10.1029/2009JD012943, 2010.

Hopper, J. F., Worthy, D. E. J., Barrie, L. A., and Trivett, N. B. A.: Atmospheric observations of aerosol black carbon, carbon dioxide and methane in the high arctic, Atmos. Environ., 28, 3047–3054, doi:10.1016/1352-2310(94)90349-2, 1994.

Sharma, S., Lavoué, D., Chachier, H., Barrie, L. A., and Gong, S. L.: Long-term trends of the black carbon concentrations in the Canadian Arctic, J. Geophys. Res.-Atmos., 109 (D15203), 1–10, doi:10.1029/2003JD004331, 2004.

Referee Comment: One final example of a finding that is perhaps misinterpreted or at least somewhat misrepresented is the attribution of PMF factor 2 to local dust. V, Se, and As are generally considered to be dominated by anthropogenic emissions, and in fact the authors point this out in their later discussion of factor 6. In particular, finding V to be enriched in Arctic Haze caused Ken Rahn to reassess, and basically refute (Rahn et al. 1985 in Atmos. Environ., see also AMAP, 2006, chapter 4), his own early suggestion that the haze was mostly dust from Asia (Rahn et al., 1977 in Nature). Mosher et al., 1993 used V to show that emissions from the generators at the DYE 3 radar station probably had a subtle but persistent impact on aerosol measurements made during the DGASP campaign. (Pretty well established that V is a tracer of oil combustion, in fact the authors point this out in discussion of factor 7.) Given the correlation between factor 2 and winds from the main station at Alert, it would seem plausible that local pollution, and not just local dust, is part of this factor.

Response: 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 7 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 measurements 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.

Referee Comment: Regarding comment about accessibility of the manuscript, the very detailed description of PMF in section 2.4.1 and section 3.1 describing how 7 factors were ultimately selected is too lengthy for a journal like ACP, especially considering that the algorithm is publicly available and presumably well described in EPA documents and Norris et al., 2014. Material in the supplemental showing the changes as additional factors are considered is well done, but not distracting to someone reading the paper who may be less interested in statistical details.

Response: We agree with the referee that a detailed description of PMF is not required within the manuscript, given the target audience of this paper. Though we do think that this information is vital to be included in all papers with PMF analyses for reproducibility and transparency. Thus, portions of section 2.4.1 and 3.1 have been moved to the supplemental.

Response to Detailed Comments

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

2/31-3/4

Referee Comment: The first paragraph of section 2.1 probably needs to be expanded to provide a few additional details about sampling and data screening. In particular, in Macdonald, 2017 the chemical fluxes in January and February were excluded in all analyses due to indications that the snow tables suffered extreme undercatch during high winds in mid winter. However, in this manuscript these data are retained, the PMF is conducted on "flux per snowfall event" rather than concentration or flux per day, and spikes in several of the factors during January and February were used to support attribution of the factor to source. Authors need to justify this pretty large change in assessment of data quality (or stick with original decision and leave mid winter out of the PMF). As noted above, I wonder if low fluxes due to snow undercatch obscured the expected winter peak in sulfate flux.

Response: Additional details on the sampling procedure have been provided in the supplemental, revised section S1. We do not believe the undercatch noted in the previous study detrimentally impacted this sourcing analysis. The composition of the snow throughout January and February is not expected to be impacted by undercatch, simply the total volume of snow. Underestimation of all analytes for a few dates does not greatly impact the apportionment of a PMF analysis, since this analysis focusses primarily on the relative variation in analytes rather than their magnitude. The profiles of the identified factors should be largely unaffected; however, the temporal flux contributions may be underestimated across all factors for the dates of interest. Furthermore, the source regions identified for each factor by weighted FLEXPART analysis may have understated the impact of source regions prevalent on those dates, but the peaks identified outside of this period should not be affected and are still valid episodes.

To better understand the impact of using snow flux instead of concentration three PMF analyses were completed: based on snow concentration, flux per period, and flux per day. The results of these auxiliary runs have been provided in this paper, moved to the supplemental per the referees' suggestions. The concentration PMF factor profiles were found to be highly consistent with those of the flux per snowfall analysis considered in the manuscript. The factor compositions agreed with Pearson's correlation coefficients of 0.97 or higher and contributions agreed with correlations of 0.60 or higher. If the uncertain January and February dates were removed the correlation of the factor contributions between the concentration and flux per snowfall PMF analyses only changed by less than 6%. Furthermore, the primary evidence used in the identification of the PMF factors in this manuscript was composition, which does not appear to have been impacted by the underestimation of flux based on undercatch in January and February.

Specifically looking at sulphate, the concentration time series is very similar to that presented for flux, with a Pearson's correlation of 0.76. Both show a very distinct fall peak with small episodic peaks in winter and spring. Neither show the typical Arctic Haze trend with a broad peak throughout the winter, as observed for BC. For reference, the concentration PMF results are provided in the supplemental and a complete record of the measured concentrations provided in Macdonald et al. (2017).

Overall, we chose to include these time periods so as to not lose potential information about sources during this important time of the year. A brief note on this topic has been added to the revised manuscript. (revised manuscript page/line(s): 3/15-17)

Figure 3

Referee Comment: Figure 3 probably needs to be modified, given its central role in attributing factors to likely sources. All 7 panels share a lot of similarities that tend to draw the eye as, or even more, strongly than small differences pointed out in the text in section 3.2. Probably the biggest problem is the bulleye very close to Alert in all of the panels. This is largely a geometric artifact reflecting that every particle released from the receptor site has to pass through a very small number of cells surrounding that site. I am pretty sure that Stohl and/or Burkhart have recognized this issue and have a recommended weighting scheme that reduces this bias (lower weights for cells closer to release site). Another minor point is that the green triangles and square in the panel for factor 7 are very hard to find (especially the Smoking Hills square). And the label under color bar should be Residence Time (not Residential), and there has to be some huge multiplier on the scale (max is not just 30 seconds)

Response: While we agree that the plots in Figure 3 do share some similarities, we do not believe this is reason to change them. We agree that the "bullseye" on Alert is the result of all tracers being initialized at this location; however, it is correct to say that Alert and the surrounding area is a significant potential source/influencing area for all factors. Reducing the weighting on this area may help in identifying long-range sources but we believe it is important to emphasize that all factors could potentially be strongly influenced by local activities. Also, we find it interesting that some factors seem to show common source/influence areas. Specifically, Factors 3, 5, and 6 all likely have anthropogenic origins and all show similar source regions, with some small exceptions. These source regions show a distinct contrast from those of Factors 1, 2, 4, and 7 which appear to be more dependent on Arctic sources/influences.

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.

The legend has been corrected to residence time. The scale has been converted to a unitless relative residence time since interpretation of the actual residence time requires information on the cell size. (revised page 10)

1/23

Referee Comment: AMAP 2011 was updated in 2017, probably should cite that report

Response: We thank the referee for this note. The reference to AMAP 2011 has been updated to the 2017 revision and this revision reviewed for any changes in relevant sections.

2/6-8

Referee Comment: Not sure how the concluding phrase about snow as a critical reservoir logically follows the first part of this sentence.

Original Line: *Particles entering the Arctic atmosphere can be removed only by atmospheric transport or deposition, and the deposition processes are much slower in the winter than in the summer; thus Arctic snow is a critical reservoir within the Arctic system.*

Response: We agree that this line was poorly phrased. The line has been revised to clarify as follows: *Particles entering the Arctic atmosphere in winter can be removed only by atmospheric transport or deposition in snow where they can be retained for an extended time; thus Arctic snow is a potentially critical reservoir within the Arctic system*. (2/17-19)

2/8-17

Referee Comment: Given the vast literature on Arctic Haze, it is unclear how the references in this section were selected. Personally, I would like to see some of the very early work cited. At a minimum, indicate that AMAP, 2006 is a review paper and readers should see references cited therein.

Response: We agree that additional sources should be included, but recognize that this is not meant to be comprehensive review paper. The following references have been added to text; furthermore, we have urged the reader to see the references within existing review papers for further information.

> Barrie, L. A.: Arctic air pollution: An overview of current knowledge, Atmos. Environ., 20 (4), 643–663, doi:10.1016/0004-6981(86)90180-0, 1986.
>
> Mitchell, J. M.: Visual range in the polar regions with particular reference to the Alaskan Arctic, J. Atmos. Terr. Phys., 17, 195–211, 1957.
>
> Rahn, K.A., Borys, R., and Shaw, G. E.: The Asian source of Arctic Haze bands, Nature, 268, 713–715, doi:10.1038/268713a0, 1977.
>
> Shaw, G., and Wendler, G.: Atmospheric turbidity measurements at McCall Glacier in northern Alaska, B. Am. Meteorol. Soc., 53 (5), 510, 1972.

3/4

Referee Comment: The last phrase after the comma is very much a matter of personal opinion. I suggest ending sentence with a period after flux (see first detailed comment above).

Original Line: *The use of a snow table allowed the deposition area associated with each sample to be recorded and used in the conversion of measured concentration to flux, which provided a considerable advantage over previous snow sampling campaigns.*

Response: This line has been revised per the referee's suggestion. (3/13-15)

3/20-21

Referee Comment: Reword this to make argument more clear, and possibly consider different wording for "under-exaggerate". Are you saying that you tossed BDL samples to make the S/N higher than it probably should have been?

Original Line: *The signal-to-noise (S/N) of each analyte was also calculated to indicate the strength of each measurement. Given the enhanced uncertainty of below MDL and missing values, these data points were excluded so as to not under-exaggerate the S/N (Norris et al., 2014).*

Response: The calculation for signal-to-noise was adopted from the EPA PMF guide (Norris et al., 2014 equation 5-3 and 5-4) and is suggested for environmental data. This approach is meant to recognize that environmental data often include some missing or even negative values which, with the older PMF4 S/N calculation, would have artificially decreased the S/N ratio. This line was revised to clarify. (4/3-6)

5/32-6/6

Referee Comment: Is this needed? Results from PCA are not shown, and appear to be mentioned in passing just once more in the manuscript (page 8, line 8)

Response: The paragraph mentioned provides a description of the principal component analysis and how it was applied to this data. As the referee notes, the results of this analysis are only provided in the supplemental and are only briefly discussed in the text. Per the referee's suggestion the bulk of this paragraph has been moved to the supplemental, section S4.3.

6/19

Referee Comment: residential-→residence

Response: Editorial comment addressed in revised text. (6/3)

9/1

Referee Comment: Enhancement of Mg above the SS ratio by a factor of 1.6 is a big difference that would suggest an additional Mg source. Same is true for SO4, but excess is expected.

Response: The enrichment of Mg^{2+} and SO_4^{2-} has been noted in the text. The enrichment of Mg^{2+} was found to be consistent even for PMF analyses with a greater number of factors which does not suggest a missing factor is responsible for the enrichment. Furthermore, similar enrichment of Mg^{2+} in a sea salt factor was also observed by Krnavek et al. (2012). The uncertainty of these enrichment ratios has been included in the text, presented as the PMF 25th and 7th bootstrapping results. (11/11-18)

> Krnavek, L., Simpson, W. R., Carlson, D., Domine, F., Douglas, T. A., and Sturm, M.: The chemical composition of surface snow in the Arctic: Examining marine, terrestrial, and atmospheric influences, Atmos. Environ., 50, 349–359, doi:10.1016/j.atmosenv.2011.11.033, 2012.

9/14-15

Referee Comment: The residence time plot suggests that the middle of the GrIS is a stronger source for this factor than Norwegian Sea or North Atlantic, probably partly due to geometric artifact mentioned earlier.

Response: It has been noted in the text that the influence of the area immediately around Alert may be over-exaggerated in Figure 3. While it is true that the Greenland ice sheet is a potential area of influence for Factor 1, the ice-free Norwegian sea and Northern Atlantic ocean are also potential areas of influence and we believe are a more probable potential source region.

10/Figure 1

Referee Comment: Please explain what the bars on this plot are showing more clearly. What is the time component indicated by "/period"?

Original Line: *Factor profiles. Error bars show the 25th and 75th percentiles of the bootstrapping analysis. Flux contributions below 0.00001 µg/m*^{2}*/period are not shown.*

Response: The percentile and mass loading to each factor is the typical method of describing PMF results. A thorough discussion of how to interpret these results is provided in the EPA PMF guide (Norris et al., 2014). However, the author recognizes that not all readers will be familiar with such analyses. For clarity, the Figure 1 caption has been revised as follows: *Factor profiles. The loading of each analyte to each factor is provided as the portion of their flux apportioned to that factor as well as the percentage of the analyte's total flux (mass/mass) apportioned to that factor. Error bars on the percentage loading show the 25th and 75th percentiles of the bootstrapping analysis. Flux contributions below 0.00001 µg/m*^{2}*/period are not shown. Metals with a charge are those measured by IC, others are insoluble portions measured by ICP-MS.* (revised page 8)

Section 3.1 paragraph one describes the flux per snowfall period metric used.

12/Figure 3

Referee Comment: Why not label the panels by source name rather than factor #?

Response: Figure 3 has been updated to include full factor names. (revised page 10)

13/29

Referee Comment: There have been a lot of papers on emissions from fires (lab, prescribed, and wild) since 2009. Liu et al., 2017 in JGR maybe most recent. This one does not include BC, but provides access to many of the papers between 2009 and 2017.

Response: This section has been revised to include references to the following more recent studies: (13/31-32)

> Liu, X., Huey, L. G., Yokelson, R. J., Selimovic, V., Simpson, I. J., Müller, M., Jimenez, J. L., et a;.: Airborne measurements of western U.S. wildfire emissions: Comparison with prescribed burning and air quality implications, J. Geophys. Res. Atmos., 122, 6108–6129, doi:10.1002/2016JD026315, 2017.
>
> May, A. A., McMeeking, G. R., Lee. T., Taylor, J. W., Craven, J. S., Burling, I., Sullivan, A. P., et al.: Aerosol emissions from prescribed fires in the United States:A synthesis of laboratory and aircraftmeasurements, J. Geophys. Res. Atmos.,119,11,826–11,849, doi:10.1002/2014JD021848, 2014.

14/1-16

Referee Comment: Hirdman et al. 2010 (2 papers, in ACP) and Stohl et al 2006 (JGR) have shown similar. They probably should be cited.

Response: The following references have been added to Section 3.2.3: (15/3)

> Hirdman, D., Burkhart, J. F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P. K., Sharma, S., Ström, J., and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the Arctic: Changes in atmospheric transport and source region emissions, Atmos. Chem. Phys., 10, 9351–9368, doi:10.5194/acp-10-9351-2010, 2010.
>
> Stohl, A., Berg, T., Burkhart, J. F., Fjæraa, A. M., Forster, C., Herber, A., Hov, Ø., et al.: Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe, Atmos. Chem. Phys., 7, 511–534, doi.org/10.5194/acp-7-511-2007, 2007.

16/1

Referee Comment: delete "both"

Response: Editorial comment addressed in revised text. (15/20)

16/3

Referee Comment: delete "to"

Response: Editorial comment addressed in revised text. (15/22)

16/3-4

Referee Comment: There have been a lot of papers on emissions from fires (lab, prescribed, and wild) since 2009. Liu et al., 2017 in JGR maybe most recent. This one does not include BC, but provides access to many of the papers between 2009 and 2017.

Response: See response to detailed comment 13/29 above.

17/11

Referee Comment: Why not say "via N2O5 hydrolysis in the aerosol phase" instead of "NO3-radical chemistry"?

Original Line: *The mid-winter peak in this factor may be linked to* NO_3^- *formation via* NO_3*-radical chemistry, which is considered to dominate Arctic* NO_3^- *chemistry during the night (Morin et al., 2008).*

Response: This line was revised as suggested. (17/1-2)

18/14

Referee Comment: Laing et al. 2014 is not original source of this fact, Rahn probably closer, but maybe even he used someone else's earlier work

Original Line: *Non-crustal Se is typically considered to be a tracer of coal combustion and V a tracer of oil combustion (Laing et al., 2014).*

Response: We agree that the original reference should be provided. The following references have been added, which we believe to be some of the earliest to discuss this topic. (18/11-12, 20/1-2)

Key, C. W., and Hoggan, G. D.: Determination of trace elements in fuel oils, Anal. Chem., 25 (11), 1673–1676, doi:10.1021/ac60083a027, 1953.

Rahn, K. A.: Sources of trace elements in aerosols – An Approach to clean air, Ph.D. thesis, University of Michigan, 1971.

18/20-21

Referee Comment: Fact that FLEXPART rarely reaches any of these volcanoes is a little problematic.

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 Báršarbunga volcano in Iceland and the Smoking Hills in Canada. (section 3.2.7)

21/7

Referee Comment: seasonally-⟶seasonal

Response: Editorial comment addressed in revised text. (22/22)

Temporally-Delineated Sources of Major Chemical Species in High Arctic Snow – Response to Anonymous Referee #2

Referee comments received and published: 25 September 2017 (quoted below in blue text)

We would like to thank Referee #2 for their detailed comments and discussion. We greatly appreciate the care with which the referee has reviewed this manuscript and the improvements gained through their insight.

Response to Referee Discussion

Referee Comment: Macdonald et al describe the results of positive matrix factorization of snow chemical composition measurement data from Alert, Nunavut in order to determine the prominent sources influencing the snow composition. Given changing Arctic source emissions with sea ice loss and increasing development, this is an important topic. A thorough description of the data analysis is provided. My main concerns, described below, surround the discussion of the results.

The main result highlighted in the abstract and conclusions is that the BC is primarily from fossil fuel burning, rather than biomass burning influence. This is not surprising since the study focuses on snow samples collected from Sept. 14, 2015 to Jun. 1, 2015, outside of the main summertime wildfire period. In several places in the paper (last paragraph of Section 3.2.3, part of Sec. 3.3, and P21 L 11-14), it is stated that these results "disagree" with previous snow chemical composition measurements that showed greater biomass burning influence, proving "contradicting snow BC apportionment findings". The authors do note the influence of seasonality and changes in annual wildfire frequency and severity on contributions of biomass burning BC. However, because the references that the authors are comparing to correspond to different times and locations, a simple comparison of the percentages of biomass burning vs fossil fuel influence is not appropriate (e.g. Table 2), without an in-depth analysis of fire locations, frequency, and timing, as well as air mass trajectories associated with the various sampling sites. I would expect that the contribution of biomass burning vs fossil fuel likely depends on the site, season, and year. Therefore, I suggest revising the discussions and comparisons to provide these results as another study that points to the variability in BC source contributions, rather than suggesting that they "disagree with" or "contradict" previous results, which gives the idea of invalidating previous work, which instead may simply be different due to different timing and location. As part of this revision of the discussion, I suggest removing Table 2, or if the authors feel strongly about keeping this comparison, then information about timing, location(s), and wildfire influence (from fire maps and air mass trajectory analysis, presumably, or statements from previous papers) should be included. In addition, a more thorough literature search is needed if the authors mean for this to be a comprehensive comparison.

Response: We agree with the referee that the discussion and tone of the listed sections should be changed. While we did try to keep our literature comparison to mostly studies of similar seasons and locations, we do agree that the sources of BC appear to be dependent on several factors. The paper has been revised to avoid statements that these results contradict those of previous studies and we instead state that they highlight the importance of understanding the variability of BC sources to Arctic snow. In general, the focus of the paper has been shifted away from BC, per the comments of the referees. Furthermore, Table 2 of the refereed document has been removed. This table was meant to be illustrative rather than comprehensive, but we agree that it is not needed.

Referee Comment: This is a complementary paper to the recent Macdonald et al (2017) ACP manuscript that describes the deposition of the same chemical species to the snowpack, with snow mixing ratios and fluxes of these species described. In that paper, Figure 1 shows time series over the same period of Sept 2014 to Jun 2015 for the following "key analytes" (as described in that paper), grouped according to time series correlations: Black carbon, methanesulfonate, C2O42- & NH4+, sea salt, NSS-sulfate, nitrate, NSS-K+ & NSS-Br-, and crustal metals; this is quite similar to the time series of the 7 factors (salt, dust, BC, carboxylic acids, nitrate, metals, and sulfate) in Figure 2 of the current paper. Despite this overlap, little discussion was included in the previous manuscript regarding likely sources.

Response: This manuscript is meant to be a companion to the previous paper (Macdonald et al., 2017) mentioned by the referee. The first paper outlines the measurements and analysis in greater detail and provides a comparison with concurrent atmospheric measurements. This paper expands on the previous, focussing on sources of these analytes to Arctic snow. Per the suggestion of the referees some additional references to the first paper and over-arching discussion have been added to the revised manuscript.

The time series provided in Macdonald et al. (2017) are grouped into related species or those with similar measured ranges, to facilitate plotting. All apportioned time series are also provided in this paper's supplemental.

> Macdonald, K. M., Sharma, S., Toom, D., Chivulescu, A., Hanna, S., Bertram, A. K., Platt, A., Elsasser, M., Huang, L., Tarasick, D., Chellman, N., McConnel, J., Bozem, H., Kunkel, D., Ying Duan, L., Evans, G. J., and Abbatt, J. P. D.: Observations of atmospheric chemical deposition to high Arctic snow, Atmos. Chem. Phys., doi:10.5194/acp-17-5775-2017, 2017.

Referee Comment: The authors are encouraged to do a more thorough literature search for previous Alert snow, aerosol, and trace gas studies that likely will support their source apportionment findings and provide evidence for greater certainty for source identification. Some appropriate papers (not meant to be comprehensive) are noted below for discussion of specific factors. While not temporally resolved, Krnavek et al 2012 (Atmos. Environ.) provide a detailed source apportionment of marine, terrestrial, and atmospheric influences on Arctic surface snow composition. Most notably, the authors do not cite or compare to Toom-Sauntry and Barrie (2002, Atmos. Environ) who previously collected weekly snow samples at Alert from 1990 to 1994 and measured inorganic and organic ions; this paper is highly relevant to the current work!

Response: The study by Toom-Sauntry and Barrie (2002) is referenced in the previous paper discussing these snow measurements (Macdonald et al., 2017). A comparison of the snow measurements from this campaign to those in previous studies, including Toom-Sauntry and Barrie 2002, is included in Macdonald et al. (2017) supplemental section S1. The trends and absolute values of major ions measured in snow in this study were mostly found to be consistent with those observed by Toom-Sauntry and Barrie, 2002. However, we agree that further discussion of how these measurements compare to those of Toom-Sauntry and Barrie within this paper is also warranted. Sections 3.2.1 and 3.2.7 have been revised to include this discussion.

We thank the referee for suggesting Krnavek et al. (2012). We have reviewed this paper and incorporated it into our discussion. We have also expanded our literature review of other related studies. The following references have been added to the manuscript:

> Barrett, T. E., Robinson, E. M. Usenko, S. and Sheesley, R. J.: Source contributions to wintertime elemental and organic carbon in the western Arctic based on radiocarbon and tracer apportionment, Environ. Sci. Technol., 49 (19), 11,631–11,639, doi:10.1021/acs.est.5b03081, 2015.
>
> Breider, T. J., Mickley, L. J., Jacob, D. J., Wang, Q., Fisher, J. A., Chang, R. Y.-W., and Alexander, B.: Annual distributions and sources of Arctic aerosol components, aerosol optical depth, and aerosol absorption, J. Geophys. Res.-Atmos., 119, 4107–4124, doi:10.1002/2013JD020996, 2014.

Doherty, S. J., Warren, S. G., Grenfell, T. C., Clarke, a. D., and Brandt, R. E.: Light-absorbing impurities in Arctic snow, Atmos. Chem. Phys., 10, 11,647–11,680, doi:10.5194/acp-10-11647-2010, 2010.

Dou, T., Xiao, C., Shindell, D. T., Liu, J., Eleftheriadis, K., Ming, J., and Qin, D.: The distribution of snow black carbon observed in the Arctic and compared to the GISS-PUCCINI model, Atmos. Chem. Phys., 12, 7,995–8,007, doi:10.5194/acp-12-7995-2012, 2012.

Hirdman, D., Burkhart, J. F., Sodemann, H., Eckhardt, S., Jefferson, A., Quinn, P. K., Sharma, S., Ström, J., and Stohl, A.: Long-term trends of black carbon and sulphate aerosol in the Arctic: Changes in atmospheric transport and source region emissions, Atmos. Chem. Phys., 10, 9351–9368, doi:10.5194/acp-10-9351-2010, 2010.

Krnavek, L., Simpson, W. R., Carlson, D., Domine, F., Douglas, T. A., and Sturm, M.: The chemical composition of surface snow in the Arctic: Examining marine, terrestrial, and atmospheric influences, Atmos. Environ., 50, 349–359, doi:10.1016/j.atmosenv.2011.11.033, 2012.

Law, K. S., Stohl, A., Quinn, P. K., Brock, C. A., Burkhart, J. F., Paris, J.-D., Ancellet, G., et al.: Arctic air pollution: New insights from POLARCAT-IPY, B. Am. Meteorol. Soc., 95 (1), 1873 – 1895, doi:10.1007/BF00138862, 2014.

McConnell, J. R., Edwards, R., Kok, G. L., Flanner, M. G., Zender, C. S., Saltzman, E. S., Banta, J. R., et al.: 20th-Century industrial black carbon emissions altered Arctic climate forcing, Science, 317, 1381–1384, doi:10.1126/science.1144856, 2007.

Pratt, K. A., Custard, K. D., Shepson, P. B., Douglas, T. A., Pöhler, D., General, S., Zielcke, J., et al.: Photochemical production of molecular bromine in Arctic surface snowpacks, Nat. Geosci., 6 (5), 351–356, doi:10.1038/ngeo1779, 2013.

Sharma, S., Ishizawa, M., Chan, D., Lavoué, D., Andrews, E., Eleftheriadis, K., and Maksyutov, S.: 16-year simulation of arctic black carbon: Transport, source contribution, and sensitivity analysis on deposition, J. Geophys. Res.-Atmos., 118, 943–964, doi:10.1029/2012JD017774, 2013.

Stohl, A., Berg, T., Burkhart, J. F., Fjæraa, A. M., Forster, C., Herber, A., Hov, Ø., et al.: Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe, Atmos. Chem. Phys., 7, 511–534, doi.org/10.5194/acp-7-511-2007, 2007.

Toom-Sauntry, D. and Barrie, L. A.: Chemical composition of snowfall in the high Arctic: 1990–1994, Atmos. Environ., 36, 2683–2693, doi:10.1016/S1352-2310(02)00115-2, 2002.

VanCuren, R. A., Cahill, T., Burkhart, J., Barnes, D., Zhao, Y., Perry, K., Cliff, S., and McConnell, J. R.: Aerosols and their sources at Summit Greenland - First results of continuous size- and time-resolved sampling, Atmos. Environ., 52, 82–97, doi:10.1016/j.atmosenv.2011.10.047, 2012

Response to Detailed Comments – Major Comments

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

The first paragraph Abstract

Referee Comment: Currently, only two results are noted here – the names of the source factors and the fossil fuel source of the BC. Can additional results associated with other factors be mentioned here to highlight this work? Also, please be consistent between the factor names here and throughout the text (e.g. this says "regional dust", but later it is discussed that the dust is likely local).

Response: Per the referees' suggestion, the abstract has been revised to briefly summarize all factors resolved rather than focussing on Factor 3, BC. 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.

Section 3.2.1 – Factor 1 (Marine Sea Salt)

Referee Comment: Is there seasonal dependence to the Br-enrichment factor? There is well-known multiphase bromine chemistry that occurs in the Arctic in the spring (see Simpson et al. 2007, ACP). Hara et al (2002, J. Geophys. Res.) conducted a detailed examination of Br- enrichments in Arctic aerosols and may be useful to consider for this work. A neutralization ratio of 0.8 is stated as neutral; what is the uncertainty associated with the calculated ratio? The discussion of the potential sea salt sources is muddled with respect to local vs far away sources and should be clarified, with improved flow in discussing the possibilities. Note that recent work has suggested that aerosols are not produced from frost flowers (Yang et al 2017, ACP; Roscoe et al 2011, J. Geophys. Res.). Were there are open leads upwind of the field site, such that open water was closer to the site? May et al. (2016, J. Geophys. Res.) pointed to sea salt production from leads in the fall-spring.

Response: Br-enrichment is observed in the spring. This observation was discussed in the previous companion paper: Macdonald et al., 2017. The time series of Br^- is provided in the supplemental, showing a broad spring peak, and mentioned in the manuscript in section 3.2.5. This peak is not well-predicted by the PMF results. Section 3.2.1 of the revised manuscript has been updated to include a brief mention of Br-enrichment.

The neutralization ratio of each factor is summarized in the revised Table 2. This table also includes the ratio calculated from the 25th and 75th bootstrapping. Factor 1 has a neutralization ratio of 0.79 with bootstrapping of 0.75 to 0.84.

Section 3.2.1 discussion has been revised to improve flow and clarity. 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. The possibility of a frost flower source has been noted as quite uncertain in the revised text. 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, so these inferences should be considered uncertain. The 0.28 correlation between Factor 1 and wind speeds has been deemed too weak to include in the revised manuscript (a minimum of 0.3 has been imposed on the values included).

Section 3.2.3 – Factor 3 (BC)

Referee Comment: The authors should consider the work of Doherty et al (2010, ACP), who measured light-absorbing impurities in ~1200 snow samples across the Arctic. Dou et al (2012, ACP) previously compared measured snow BC to simulations of the spatial distribution of snow BC using the GISS-PUCCINI model. Recently, Barrett et al (2015, Environ. Sci. Technol.) used radiocarbon tracers to determine elemental carbon source apportionment between modern and fossil fuel carbon at Barrow, AK; perhaps some discussion in that work may be helpful here.

Response: The suggested references have been added to section 3.2.3.

Section 3.2.4 – Factor 4 (Carboxylic Acids)

Referee Comment: In the authors' consideration of carboxylic acid sources, they should consult the work of Narukawa et al (2002, Atmos. Environ.) who measured aerosol and surface snowpack dicarboxylic acids at Alert in Feb and April-May 2000. Dibb and Arsenault (2002, Atmos. Environ.) examine snow as a source of acetic and formic acids.

Response: Narukawa, Kawamura, and Bottenheim (2002) explored dicarboxylic acid measurements in Arctic aerosol and surface snowpack. Given that this campaign did not include measurements of formate and/or acetate which are the dominant components of Factor 4, we have decided not to include it in the discussion. However, we thank the referee for his suggestion.

The Dibb and Arsenault (2002) paper mentioned is already included in this discussion. (16/1-2)

> Dibb, J. E. and Arsenault, M.: Shouldn't snowpacks be sources of monocarboxylic acids?, Atmos. Environ., 36, 2513–2522, doi:10.1016/S1352-2310(02)00131-0, 2002.

Section 3.2.5 – Factor 5 (Nitrate)

Referee Comment: The authors cite Morin et al (2008) and Fibiger et al (2016) for nitrate cycling associated with the snowpack. However, Fibiger et al (2016) is a study at Summit, Greenland. There are other appropriate studies at Alert that should be considered in the context of the current work – for example, Ianniello et al (2002, Atmos. Environ) and Beine et al (2002, Atmos. Environ.).

Response: The suggested references have been added to the manuscript:

> Beine, H. J., Honrath, R. E., Domine, F., and Simpson, W. R.: NOx during background and ozone depletion periods at Alert: Fluxes above the snow surface, J. Geophys. Res., 107 (D21), 7-1–7-12, doi:10.1029/2002JD002082, 2002.
>
> Ianniello, A., Beine, H. J., Sparapani, R., Di Bari, F., Allegrini, I., and Fuentes, J. D.: Denuder measurements of gas and aerosol species above Arctic snow surfaces at Alert 2000, Atmos. Environ., 36 (34), 5,299–5,309, doi:10.1016/S1352-2310(02)00646-5, 2002.

Section 3.2.7 – Factor 7 (Sulfate)

Referee Comment: In considering the main sources of snow sulfate, the authors should consult the work of Norman et al (1999, J. Geophys. Res.) who used sulfur isotopes to determine seasonal aerosol sulfate sources at Alert from July 1993 to Sept. 1994. The authors note that several volcanoes were active over the 2014-2015 season. This factor peaks in the early fall; does this coincide with the volcano activity and associated air mass trajectories (FLEXPART analysis)? Reorganize this section so that there is a clear flow of discussion – currently the authors go back and forth between multiple potential sources. For example, L20-21 and 27-29 seem to be somewhat contradictory as written. L6-7 on P19 seems to be tacked on and should be integrated.

Response: Sirois and Barrie (1999), the companion paper to Norman et al. (1999) provides further analysis of aerosol sources. This study is cited within the manuscript.

Section 3.2.7 has been revised to improve flow and clarity. The text does state that Bárðarbunga, a volcano in Iceland, was active during the observed fall peak. The revised section gives details on how this compares with the FLEXPART analysis. Lines 20-21 and 27-29 of the original manuscript have been removed in the revision.

Section 3.3

Referee Comment: This section is labeled as “Overall Apportionment”, but it is really primarily a discussion of how BC is apportioned between the factors. It may be useful to rename the title of this section, or reorganize and revise the section to make it more evenly about all of the factors. I would suggest a paragraph break at L21, with some reorganization between the two paragraphs. The authors point to mixing state of the particles potentially being important (L23-25), and this could be strengthened by citing previous Arctic studies (e.g. Weinbrunch et al 2012, Atmos. Environ.).

Response: Section 3.3 has been heavily revised to include greater discussion of all factors and reduce focus on Factor 3, BC. The apportionment of all analytes has been summarized in the revised Table 3. Figure 4 has also been expanded to show the apportionment of BC, SO_4^{2-}, and insoluble V.

Table 3

Referee Comment: It would be useful to integrate these results into the prior factor discussions (section 3.2).

Response: Per the referee’s suggestion Table 3 has been moved to revised section 3.2. (now Table 2).

Conclusions

Referee Comment: The conclusions are very general, with limited discussion of any factor or analyte other than BC. There is an opportunity here to discuss other factors and analytes, particularly with respect to how they may change in the future, or with respect to uncertainties that should be examined in future work.

Response: The conclusions have been revised to discuss other factors and analytes in greater detail.

Response to Detailed Comments – Minor Comments and Technical Corrections

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

1/19, 8/13, and other locations

Referee Comment: Please clarify text to describe the units used for calculating the percentage. I assume for BC that you are calculating the % based on mass conc? For Na+, for example, are you reporting the fraction of Na+ measured in the snow that was apportioned to the first factor? This isn't currently clear and could be worried more clearly throughout the manuscript where percentages are used.

Response: The referee is referring to the percentile loadings of various analytes onto each PMF factor. This represents the portion of total analyte mass apportioned to a single factor. To clarify, "mass/mass" has been added where appropriate, and the first use has been described as follows: *The first factor was characterized by high loadings (>75% of total flux mass apportioned to Factor 1) of* Na^+ *and* Cl^- *and 30-45% loadings of* Br^-, K^+, *and* Mg^{2+} *(Figure 1; Table 2).* (revised manuscript page/line(s): 11/8-10)

1/19

Referee Comment: Fix phrasing/sentence structure as snow is not a light-absorbing compound.

Original Line: *The majority (73%) of the black carbon in snow, a light-absorbing compound critical to the Arctic radiative balance, was found to be the product of fossil fuel burning with limited biomass burning influence.*

Response: Per the comment above, the abstract has been revised to provide further details about all factors, with less focus on BC. The line above has been removed from the revised abstract.

2/7-10 & 14-15, 15/15, and 17/8-9

Referee Comment: Provide references.

Original Lines:

2/7-10: *Particles entering the Arctic atmosphere can be removed only by atmospheric transport or deposition, and the deposition processes are much slower in the winter than in the summer; thus Arctic snow is a critical reservoir within the Arctic system. Given the seasonal variability in Arctic aerosol inputs and outputs, a period of enhanced accumulation is typically experienced during the Arctic winter and early spring termed "Arctic Haze".*

2/14-15: *However, direct* measurements *of pollutants in Arctic snow have been less common, particularly sampling campaigns of fresh snow which are less prone to the ambiguities introduced by snowpack collection.*

15/15: *Possible contributors hypothesized in other studies of arctic carboxylic acids are discussed below including biomass burning, atmospheric or snow photochemical processing, and ocean microlayer emissions.*

17/8-9: *February to June, 2015, was also characterized by a "bromide explosion", observed as a broad peak in snow and atmospheric* Br^-.

Response: The following reference has been noted to the revised manuscript for Line 2/7-10 (revised page/line: 2/19)

> AMAP: Acidifying pollutants, Arctic haze, and acidification in the Arctic, Arctic Monitoring and Assessment Programme, Oslo, Norway, 2006.

Line 2/14-15 has been revised as follows: "*However, direct measurements of pollutants in Arctic snow have been less common, particularly sampling campaigns of fresh snow.*" per the comment below. (2/26-27)

Line 15/15 is simply listing topics that will be discussed in the following section. The following references are provided in the following discussion:

> Jaffrezo, J.-L., Davidson, C. I., Kuhns, H. D., Bergin, M. H., Hillamo, R., Maenhaut, W., Kahl, J. W., and Harris, J. M.: Biomass burning signatures in the atmosphere of central Greenland, J. Geophys. Res., 103, (D23), 31067-3108, doi:10.1029/98JD02241, 1998.
>
> Legrand, M., and de Angelis, M.: Origins and variations of light carboxylic acids in polar precipitation, J. Geophys. Res., 100 (Di), 1445–1462, doi:10.1029/94jd02614, 1995.

The following reference has been noted to the revised manuscript for Line 17/8-9 (16/32-33)

> Macdonald, K. M., Sharma, S., Toom, D., Chivulescu, A., Hanna, S., Bertram, A. K., Platt, A., Elsasser, M., Huang, L., Tarasick, D., Chellman, N., McConnel, J., Bozem, H., Kunkel, D., Ying Duan, L., Evans, G. J., and Abbatt, J. P. D.: Observations of atmospheric chemical deposition to high Arctic snow, Atmos. Chem. Phys., doi:10.5194/acp-17-5775-2017, 2017.

2/15

Referee Comment: Please clarify the phrase "less prone to the ambiguities introduced by snow-pack collection".

Response: A comparison of fresh and aged snow sampling was discussed in the previous paper. However, we agree that this line should not be included here without additional clarification or references. In the interest of space, this line has been removed from the revised manuscript.

2/27-28

Referee Comment: Mention measurements data here – otherwise it sounds like the study includes only PMF and air mass modeling.

Original Line: *In this context, this paper analyses the sources of chemical components in freshly-fallen snow samples collected over a complete fall-winter-spring at a high Arctic location (Alert, Nunavut), using a combination of Positive Matrix Factorization diagnostics and Lagrangian dispersion modelling.*

Response: The line has been revised as suggested: "*In this context, this paper analyses the sources of chemical components in freshly-fallen snow samples collected over a complete fall-winter-spring at a high Arctic location (Alert, Nunavut) and analysed for a broad suite of analytes, using a combination of Positive Matrix Factorization diagnostics and Lagrangian dispersion modelling.*" (3/4-7)

7/3

Referee Comment: Is this supposed to be 59 samples (based on P3 L2)?

Response: The referee is correct that a total of 59 sets of samples were analysed in the course of this study; however, some collection periods did not provide sufficient snow volume to perform the complete suite of analyses (see referenced Macdonald et al., 2017 for the complete list of sampling dates, completed analyses, and results). Section 2.4.1 of the manuscript explains that the PMF analysis was limited to collection periods with the majority of analytes of interest measured (original manuscript 5/21; revised manuscript 5/12).

7/4

Referee Comment: Clarify wording that you are discussing analyte concentrations and fluxes.

Original Line: *Three metrics were considered as the basis for this analysis: snow concentration, flux per day, and flux per snowfall (i.e., assuming each sample represented a single snowfall event regardless of the time period over which it occurred, which is known to be true for the majority of samples based on Alert station operator records).*

Response: The line has been revised to clarify as follows: *Three metrics were considered as the basis for this analysis: analyte concentration, flux per day, and flux per snowfall (i.e., assuming each sample represented a single snowfall event regardless of the time period over which it occurred, which is known to be true for the majority of samples based on Alert station operator records).* Per the referees' suggestions, details on the PMF analysis have been largely moved to the supplemental, including this line. (revised supplemental page 10)

7/13-14

Referee Comment: This discussion is not intuitive and could be clarified further. Can we learn about processes from these differences?

Original Line: *The source contributions identified by the flux per snowfall period analysis were the most readily interpreted as physically realistic factors. Moreover, this metric showed the largest correlation between BC snow and atmospheric measurements (Pearson's correlation coefficients of 0.4, 0.3, and 0.5 for BC concentration, flux per day, and flux per snowfall period, respectively), implying that the flux per snowfall may in general be more closely related to the change in analyte sources over time while concentration and flux per day may be more intrinsically dependent on changes in deposition processes.*

Response: Per the referee comments, discussion of the concentration and flux/day PMF analyses has been moved from the manuscript to the supplemental. The following has been added to this discussion in the supplemental to clarify: "*For example flux per snowfall is likely related to a specific synoptic event, arising from a common location. This will be more useful than concentration given that this value will be affected by the amount of precipitation, and more useful than flux per day that will be affected by the rapidity of snowfall.*" (revised supplemental page 10-11)

7/17-33, 8/5-9, and Table 1

Referee Comment: I suggest moving these paragraphs to the methods and supplementary information, as they discuss how the authors decided to use seven factors and do not discuss science. The section is also difficult to follow without in-depth knowledge of the method, and without referring back to the methods section frequently. Similarly, I suggest moving Table 1 to the supplementary information.

Response: Per the referee's suggestion, this section has been shortened in the manuscript. Table 1 has been left in the manuscript as it lists the analytes included in the PMF analysis and specifically which were considered strong or weak. We agree that the diagnostic properties are not necessary in the manuscript for the target audience of the ACP; however, we do believe it is important to list the analysis main inputs and describe the overall fit of the predicted results.

8/14-15

Referee Comment: These sentences are redundant.

Original Line: *These compounds are all typical of sea salt, suggesting a marine origin for Factor 1. The composition of Factor 1 was found to be consistent with that of sea salt (Pytkowicz and Kester, 1971).*

Response: The intention of these two lines was to convey that the dominant compounds as well as their relative proportions were both consistent with a marine source. We agree that as written this distinction is not clear and the lines become redundant. The line has been revised as follows: *These dominant analytes and their relative proportions are consistent with that of sea salt (Pytkowicz and Kester, 1971), suggesting a marine origin for Factor 1*. (11/10-11)

9/1-12

Referee Comment: "Compound(s)" should be "ion(s)" here. Also, what are the uncertainties in the enrichment ratios? (These errors should be stated for all enrichment ratios reported in this manuscript.)

Response: The word "compounds" has been removed, and typically replaced with "analytes" as to be general. The uncertainty of enrichment ratios have been described in the text using the 25th and 75th bootstrapping analysis results. (11/8-12/3)

Figure 1

Referee Comment: Remove "(point)" and "(bar)" on the y axes, as this is already shown in the legend, and "bar" is a unit of pressure.

Response: Addressed in revised manuscript.

Figure 1 Caption

Referee Comment: Provide further description of how to interpret the figure for improved clarity, particularly for those not familiar with PMF.

Original Line: *Factor profiles. Error bars show the 25th and 75th percentiles of the bootstrapping analysis. Flux contributions below 0.00001 $\mu g/m^2$/period are not shown.*

Response: The percentile and mass loading to each factor is the typical method of describing PMF results. A thorough discussion of how to interpret these results is provided in the EPA PMF guide (Norris et al., 2014). However, the authors recognize that not all readers will be familiar with such analyses. For clarity, the Figure 1 caption has been revised as follows: *Factor profiles. The loading of each analyte to each factor is provided as the portion of their flux apportioned to that factor as well as the percentage of the analyte's total flux (mass/mass) apportioned to that factor. Error bars on the percentage loading show the 25th and 75th percentiles of the bootstrapping analysis. Flux contributions below 0.00001 $\mu g/m^2$/period are not shown.* (revised page 8)

Figure 2 Caption

Referee Comment: What are the traces normalized to (themselves, other factors?)? What are the units? This caption is not clear.

Response: Normalized factor contribution is the metric provided directly by the EPA PMF analysis and is the typical method used to discuss these results. A thorough discussion of this metric and its interpretation are provided in the EPA PMF guide (Norris et al., 2014). However, the authors recognize that not all readers will be familiar with such analyses. For clarity, the Figure 2 caption has been revised as follows: *Normalized factor contribution. The unitless contributions describe the relative magnitude of each factor over time such that the average contribution of each factor is one*. (revised page 9)

11/9

Referee Comment: Provide the calculated ratio in parentheses for context.

Original Line: *Specifically, the modelled ratio of As/Al was seen to be closer to that of local soils (Barrie, den Hartog, and Bottenheim, 1989) than the global typical composition (Taylor, 1964; Masson-Delmotte et al., 2013) with enrichment ratios of 6 and 37, respectively.*

Response: This primary focus of this line is to convey the greater similarity of the apportioned factor to local soil as compared to typical global soils. This is exemplified with the enrichment ratios provided. The line has been revised to also provide the ratios as follows: *Specifically, the modelled ratio of As/Al (0.00081 m/m) was seen to be closer to that of local soils (0.00013) (Barrie, den Hartog, and Bottenheim, 1989) than the global typical composition (0.00002) (Taylor, 1964; Masson-Delmotte et al., 2013) with enrichment ratios of 6 and 37, respectively (6.3-9.5 and 37-58 25th-75th percentiles per bootstrapping analysis).* (12/28-31)

13/32

Referee Comment: The neutralization equation is provided on P9, but it is not clear if the same equation is used for the calculation here and elsewhere in the paper.

Response: The updated manuscript provides all neutralization ratios in the revised Table 2. It is clarified that the provided formula is used for all calculations. (9/8-11)

Table 3

Referee Comment: While there is a footnote defining "Southern Oceans", I suggest renaming to Atlantic & Pacific Oceans, since "Southern Ocean" is a phrase typically referring to near the Antarctic.

Response: We agree that the original naming could be misconstrued. This has been revised as "Open Ocean". (revised page 11)

Figure 4

Referee Comment: The abbreviation "Cbx. Ac." In the legend is not immediately obvious; I suggested writing out "carboxylic acids" on two lines instead for improved clarity.

Response: Figure revised with "carboxylic acid" as legend entry. (revised page 10)

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 in blue text)

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.

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 measurements 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 Bárðarbunga 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.

Temporally-Delineated Sources of Major Chemical Species in High Arctic Snow

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Abstract. Long-range transport of aerosol from lower latitudes to the high Arctic may be a significant contributor to climate forcing in the Arctic. To identify the sources of key contaminants entering the Canadian high Arctic an intensive campaign of snow sampling was completed at Alert, Nunavut, from September 2014 to June 2015. Fresh snow samples collected every few days were analysed for black carbon, major ions, and metals, and this rich data provided an opportunity for a temporally-refined source apportionment of snow composition via Positive Matrix Factorization in conjunction with FLEXPART potential emission sensitivity analysis. ~~Seven source factors were identified: sea salt, regional dust, Eurasian fossil fuel combustion, North American biomass burning/cloud processing, nitrate processing, Eurasian industrial activities, and regional volcanic and marine biogenic activity. The majority (73%) of the black carbon in snow, a light-absorbing compound critical to the Arctic radiative balance, was found to be the product of fossil fuel burning with limited biomass burning influence.~~Seven source factors were identified: sea salt, crustal metals, black carbon, carboxylic acids, nitrate, non-crustal metals, and sulphate. The sea salt and crustal factors showed good agreement with expected composition and primarily northern sources. High loadings of V and Se onto Factor 2, crustal metals, was consistent with expected elemental ratios, implying these metals were not primarily anthropogenic in origin. Factor 3, black carbon, was an acidic factor dominated by black carbon but with some sulphate contribution over the winter-haze season. The lack of K^+ associated with this factor, Eurasian source, and limited known forest fire events coincident with this factor's peak suggested a predominantly anthropogenic combustion source. Factor 4, carboxylic acids, was dominated by formate and acetate with a moderate correlation to available sunlight and an oceanic/North American source. A robust identification of this factor was not possible; however atmospheric photo-chemical reactions, ocean microlayer reaction, and biomass burning were explored as potential contributors. Factor 5, nitrate, was an acidic factor dominated by NO_3^-, with a likely Eurasian source and mid-winter peak. The isolation of NO_3^- on a separate factor may reflect its complex atmospheric processing, though the associated source region suggests possibly anthropogenic precursors. Factor 6, non-crustal metals, showed heightened loadings of Sb, Pb, and As, and correlation with other metals traditionally associated with industrial activities. Similar to Factors 3 and 5, this factor appeared to be largely Eurasian in

origin. Factor 7, sulphate, was dominated by SO_4^{2-} and MSA with a fall peak and high acidity. Coincident volcanic activity and northern source regions may suggest a processed SO_2 source of this factor.

1 Introduction and Background

Observations of Arctic climate have shown pronounced changes over recent years, including a rapid rise in surface temperature and the loss of sea ice and snow cover, with adverse local and global consequences (AMAP, ~~2011~~2017; Hartmann et al., 2013). Such changes in Arctic climate have been tied to contaminants within the Arctic atmosphere and snow, especially light absorbing compounds such as black carbon (BC) which can warm the surface and atmosphere (Clarke and Noone, 1985; Hansen and Nazarenko, 2004; Bond et al., 2013; Jiao et al., 2014). Furthermore, studies have found the long-range transport of lower-latitude anthropogenic and natural emissions to be a significant and substantial contributor to the Arctic aerosol burden (Stohl, 2006; Law and Stohl, 2007; AMAP, 2015). Thus, understanding the sources of these pollutants is a critical step in the development of control and mitigation strategies to protect the vulnerable Arctic environment.

The lower troposphere of the Arctic is separated from the upper and southerly atmosphere by a transport barrier known as the "Arctic front" or "Arctic dome". This dome is formed by surfaces of constant potential temperature, which inhibit the transport of southerly air masses into the lower Arctic troposphere, instead forcing northward-travelling air masses to rise over the dome. The size and location of the Arctic front is a complex system driven by global atmospheric conditions, with significant variation by season. Over the summer, the Arctic front is typically northward of 70 °N; however, during the winter the Arctic front extends farther south, as far as 40 °N (Stohl, 2006; Law and Stohl, 2007; AMAP, 2015). The Arctic front is also zonally asymmetric, typically extending much farther south over Eurasia during the winter. Thus, the Arctic atmosphere is more vulnerable to transport from southerly sources in the winter than the summer, especially Eurasian sources. Particles entering the Arctic atmosphere in winter can be removed only by atmospheric transport or deposition~~, and the deposition processes are much slower in the winter than~~ in ~~the summer~~snow where they can be retained for an extended time; thus, Arctic snow is a potentially critical reservoir within the Arctic system~~.~~ (AMAP, 2006). Given the seasonal variability in Arctic aerosol inputs and outputs, a period of enhanced accumulation is typically experienced during the Arctic winter and early spring termed "Arctic Haze". The haze is primarily composed of sulphate (SO_4^{2-}) and organic particulate matter with varying levels of ammonium (NH_4^+), nitrate (NO_3^-), mineral dust, and BC (Mitchell, 1957; Shaw and Wendler, 1972; Rahn, Borys, and Shaw, 1977; Barrie, 1986; AMAP, 2006; Quinn et al., 2007; and the references therein).

Interest in Arctic aerosol increased after the first observations of Arctic Haze in the 1950's (Mitchell, 1957; AMAP, 2006), and intensive routine monitoring of the Arctic atmosphere dates back to the late 1970's, particularly monitoring of BC and SO_4^{2-} (Barrie, Hoff, and Daggupaty, 1981). However, direct measurements of pollutants in Arctic snow have been less common, particularly sampling campaigns of fresh snow~~ which are less prone to the ambiguities introduced by snowpack collection.~~. The relative abundance of Arctic aerosol data has facilitated extensive research on particulate sources (e.g., Sirois and Barrie, 1999; Stohl et al., 2013; Nguyen et al., 2013; Yttri et al., 2014). Fewer studies have identified the sources of snow impurities, which represent the deposited and surface albedo-influencing portion of the aerosol, and often these studies are reliant on modelled snow concentrations (e.g., Skeie et al., 2011; Wang et al., 2011) rather than measurements (e.g., Hegg et al., 2009; Hegg et al., 2010). Also,~~ great~~ variability has been seen across existing snow apportionment studies. For example, previous studies show significant disagreement in the apportionment of BC during the Arctic winter, ranging from approximately 10% to over 90% attributed to biomass burning (e.g., Wang et al., 2011 and e.g., Hegg et al., 2009, respectively). To the best of the authors' knowledge, no quantitative source apportionment has previously been conducted using temporally-refined fresh Arctic snow samples. Given the critical consequences arising from the deposition of BC and other impurities in snow, source apportionment specifically of these deposited chemical species is an important step towards understanding the Arctic environment. In this context, this paper ~~analyses~~analyzes the sources of chemical components in freshly-fallen snow samples collected over a complete fall-winter-spring at a high Arctic location (Alert, Nunavut~~),~~) and analyzed for a broad suite of analytes, using a combination of Positive Matrix Factorization diagnostics and Lagrangian dispersion modelling.

2 Methodology

2.1 Snow Sample Collection and Analysis

Sample collection and analysis was completed as per Macdonald et al. (~~2017).~~2017). Briefly, fresh snow samples were collected at Alert, Nunavut (82°30' N, 62°20' W), from September 14th, 2014 to June 1st, 2015 from two snow tables located in an open-air minimal traffic site, about 1 km SSW of the Alert base camp. Replicate samples were collected after each snowfall, weather permitting, to a total of 59 sets of samples ranging from 1 to 19 days between samples with an average of 4 days. The use of a snow table allowed the deposition area associated with each sample to be recorded and used along with sample volume in the conversion of measured concentration to flux~~, which provided a considerable advantage over previous~~. High winds in January and February may have led to undercatch of snow on the snow tables, under-estimating the calculated flux; however, snow composition measurements on these dates is not believed to have been impacted. Further details on the sampling ~~campaigns~~methodology are provided in the supplemental section S1.

Snow samples were analysed for BC via single particle soot photometry (SP2), major ions via ion chromatography (IC) and pH analyzer, and soluble and insoluble metals via inductively coupled plasma mass spectrometry (ICP-MS~~) as described~~). A summary of the analysis methodology is provided in supplemental section S1.2, with further detail provided in Macdonald et al. (2017). Stringent quality assurances were followed throughout snow collection and analysis. The uncertainty of each measurement was estimated based on analysis detection limits and reproducibility as follows (Reff et al., 2007; Norris et al., 2014):

$$u_{ij} = \sqrt{\left(EF_j \; x_{ij} \right)^2 + \left(\tfrac{1}{2} \; MDL_j \right)^2} \quad , if \; x_{ij} \; \geq \; MDL_j \tag{1}$$

$$u_{ij} = \tfrac{5}{6} \; MDL_j \quad , if \; x_{ij} \; < \; MDL_j$$

$$u_{ij} = \; 4 \, \bar{X}_j \quad , if \; x_{ij} \; is \; missing$$

where x_{ij} is the i^{th} measured value of analyte j, u_{ij} is the uncertainty associated with this measurement, EF_j is the error fraction for this analyte, $\bar{X}_j$ is the median measurement for this analyte, and MDL_j is the method detection limit for this analyte.

The error fraction of each analyte was calculated as double the standard error of replicate measurements for each analysis, with a minimum of 10% imposed (Macdonald et al., 2017 as per Hegg et al., 2010). The method detection limit of each analyte was calculated as three standard deviations of analyzed blank samples. The uncertainty for any samples with known preparation concerns was doubled (e.g., partial sample melt in transit or poor mass closure over preparation); however, less than 7% of samples were noted as having potential preparation concerns.

The signal-to-noise (S/N) of each analyte was also calculated to indicate the strength of each measurement. Given the enhanced uncertainty of below MDL and missing values, these data points were excluded ~~so as to not under-exaggerate~~from the ~~S/N (~~analysis per the suggestion of Norris et al~~.,~~. (2014~~).~~) for environmental data. A S/N over 2 was considered to be strong, while a S/N from 0.2 to 2 was considered weak (Paatero and Hopke, 2003).

$$S/N_j = \tfrac{1}{n} \sum_{i=1}^{n} d_{ij} \quad ; \tag{2}$$

$$d_{ij} = \frac{x_{ij} - u_{ij}}{u_{ij}} \quad , if \; x_{ij} > u_{ij}$$

$$d_{ij} = \; 0 \quad , if \; x_{ij} \; < \; u_{ij}$$

where S/N_j is the signal-to-noise of analyte j, n is the total number of samples, and d_{ij} is a measure of the difference between the measured value and its uncertainty for the i^{th} measurement of this analyte (all other variables are defined as in Eq. 1).

To complement snow measurements, simultaneous meteorological and atmospheric aerosol measurements throughout the campaign were considered, as provided by Environment and Climate Change Canada (ECCC). Local meteorological conditions were monitored by the Alert ECCC stations (Climate IDs 2400306, 2400305, and 2400302) (retrieved Nov. 2015 from climate.weather.gc.ca). Atmospheric composition was monitored at the Alert base camp: BC via hourly SP2 and major ions via IC of 6 to 8-day high-volume filters of total suspended particles (Hi-Vol). All ~~the~~ data are presented in ~~our~~an earlier publication (Macdonald et al., 2017).

2.4 Computational Analyses

Two approaches to source identification were used. Source type was explored via measurement apportionment to identify the source composition and seasonal contribution. Source location was explored via backward particle dispersion modelling.

2.4.1 Source Apportionment

Positive matrix factorization (PMF) is a numerical technique for describing speciated data as factors with associated compositional and temporal profiles. ~~Unlike many other source apportionment methods, PMF offers the distinct advantages of enforced positive factor solutions and weighting of the solution by user defined uncertainties. This allows realistic interpretation of the solution and the ability to determine the control that individual measurements have over the optimal solution (Norris et al., 2014).~~ This study uses the most recent US EPA version, PMF5, which uses the multilinear engine ME2 to solve the following equation set (Norris et al., 2014):

$$X = G \cdot F + E \quad , \quad x_{ij} = \sum_{p=1}^{q} g_{ip} \cdot f_{pj} + e_{ij} \quad ; \tag{3}$$

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \quad ,$$

where X is the n by m matrix of measurements with associated uncertainties u, G is the calculated n by q matrix of factor contributions, F is the calculated q by m matrix of factor compositions, E is the n by m error matrix, with lower case variables representing the specific value therein for the i^th^ sample of the j^th^ analyte for the p^th^ factor, and Q is the object function.

So, for any dataset with n measurements of m analytes a solution is found for the matrices G and F for a particular number of factors, p, which produces the minimum value of Q, an optimization parameter calculated as the summed residual error, e, weighted by the measurement uncertainty, u. ~~The Q value can be calculated via two different modes: true (Q_{true}) or robust (Q_{rob}). These modes are identical except that the robust mode of analysis excludes measurements from the calculation of Q if they have a $^{e_{ij}}/_{u_{ij}}$ value greater than 4; thus, the robust mode reduces the impact of outliers. The robust mode was used for this analysis as it is better suited for environmental data which may not be normally distributed (Norris et al., 2014).~~ An additional 10% uncertainty was applied to all measurements in the PMF analysis, beyond that uncertainty captured in Eq. 1, to account for extra modelling uncertainty and further reduce the impact of noise. Any missing measurements were replaced with the median measured value (Norris et al., 2014).

~~Selection of~~To determine the optimal number of factors~~ is a critical step of a PMF analysis. Trial~~, p, trial runs ranging from 2 to 9 factors were completed using 100 distinct random seeds per run. ~~This study used five considerations during the selection of an optimal number of factors. Firstly, the~~Trials were compared in terms of relative Q-value, improvement ~~in Q_{rob} observed~~ of solution with ~~the addition of a~~each additional factor~~ was calculated. The addition of another factor should improve the calculated Q_{rob} value to be considered a viable factor. Secondly, the solution's Q_{rob} was compared to the expected value of Q, calculated as follows (Norris et al., 2014):~~

~~$Q_{exp} = nm - (pn + pm)$, (4)~~

~~where Q_{exp} is the expected value of Q and all other variables are as described in Eq. 3, considering only strong analytes.~~

~~A ratio of Q_{rob} to Q_{exp} of one was considered ideal. Thirdly, the~~ , solution reproducibility~~ of the solution was examined such that solutions with greater reproducibility among the 100 seeded calculations for each run were given more consideration. Fourthly, the fit of each potential solution was considered. The residuals of each analyte were examined for each potential~~, solution ~~to ensure that they were normally distributed and with a minimal number of normalized residual values greater than 3 across all samples and analytes. Also, the correlation of predicted and measured values was calculated for all analytes. Finally, the~~ fit, and solution interpretability~~ of each solution was considered.~~. Only solutions which produced factor profiles which could be explained in a real-world setting were considered. Random error and rotational ambiguity of the selected solution was explored by rerunning with 500 seeds, analysis of G-space plots, and quantification via the bootstrap error model. Supplemental section S1.2 provides further details on the PMF analysis.

~~The selected optimal solution was repeated with the number of seeds increased to 500 to insure detection of the global minimum and the rotational ambiguity of this solution was then considered. For a given solution, there are several possible G and F matrices defined as rotations of the original solution. The rotation which produced the minimum value of Q was found. Furthermore, G-space plots, which compare the contribution of individual factors to each sample, where examined for the various rotation options. The factors identified by a solution should be independent, i.e., show no relationship on a G-space plot. Also, random error and rotational ambiguity of the PMF solution were quantified using a bootstrap error model with the default parameter settings: block size = 4, number of bootstraps = 50, and minimum correlation R-value = 0.6. Three error models are available with PMF5, but the bootstrap model has been recommended for data where the uncertainties are not well-known (Paatero et al., 2014).~~

The number of measurements included, n, was limited to dates with sufficient snowfall to complete the majority of analyses. Given the limited number of snow samples measurements available, a subset of the analyzed chemical species was used for PMF analysis. Only analytes with over 60% of measurements above MDL and strong S/N were included in the analysis. Analytes of particular interest to this study with sufficient S/N but only 30-60% of measurements greater than MDL were included in some cases but defined as weak variables (i.e., user-defined uncertainty was tripled for these analytes). Analytes which duplicated others were also excluded from the PMF analysis, such as analytes measured by two methods (e.g., IC and ICP-MS overlapping analytes) and analytes which are expected to share a common source and show extremely strong correlations (e.g., crustal metals with no significant anthropogenic source). Duplicate and closely related analytes do not provide additional information to the apportionment study but artificially inflate the importance of these analytes and increase the ratio of analytes to measurements unnecessarily. The complete list of chemical species included in each analysis is provided with the results.

~~The relatively small number of samples available for this study was a concern, despite analyte exclusion. Therefore, a simplified supplementary principal component analysis (PCA) was completed to corroborate the PMF results. PCA has been described in detail by others (e.g., Henry et al., 1984). Briefly, PCA describes the measured data as a set of eigenvectors, termed principal components, which each describe a portion of the observed variance. These eigenvectors and their associated eigenvalues were calculated from the correlation matrix of the measured analytes. There is no non-negativity constraint on the principal components identified by PCA as there is for PMF, nor does PCA provide quantitative factor loadings. Furthermore, PCA does not include measurement weighting by uncertainty and is therefore more sensitive to missing and below MDL~~

~~values than PMF. Thus, the results of PCA are less conducive to realistic interpretations and were used only as validation of the PMF results. No rotation or error estimates were made for the PCA.~~

2.4.2 Transport Modelling

The Lagrangian particle dispersion model FLEXPART, described in detail by Stohl et al. (2005), has been shown to be an effective tool for the prediction of transport pathways into and within the Arctic (e.g., Stohl, 2006; Paris et al., 2009). This potential emission sensitivity analysis was completed to identify likely source locations, as a complement to the PMF descriptions of source type. Modelled tracers were initialized over Alert and tracked backwards in time over a ten-day period at a 3-hr time step, driven using operational analysis data from the European Centre for Medium-Range Weather Forecasts with a horizontal resolution of 0.25° in longitude and latitude and 137 vertical hybrid pressure levels. Tracers were initialized at four altitudes over Alert: 100 m, 500m, 1000 m, and 2000 m above sea level. A simulation was completed for every 5 days over the campaign. Simulation results provided the expected residence time of the tracers at the horizontal resolution of the meteorological input data and on 10 levels up to 10 km.

The potential FLEXPART source regions associated with each PMF factor were identified. The peak periods associated with each factor, selected as the top 90th percentile of the factor contribution time series, were used to weight the FLEXPART ten-day ~~residential~~residence times over the campaign , as per Eq. ~~5~~4:

$$t_p^{xy} = \frac{\sum_{i=1}^{n} g'_{ip}\, t_i^{xy}}{\sum_{i=1}^{n} g'_{ip}} \qquad (~~5~~4)$$

$$g'_{ip} = g_{ip} \;\; , if\; g_{ip} \geq g_p^{90} \;\; else, \;\; g'_{ip} = 0$$

where t_p^{xy} is the residence time at location x,y for pth PMF factor, t_i^{xy} is the ith residence time at location x,y, g_{ip}' is the 90th percentile contributions of the pth factor at time i, g_p^{90} is the 90th percentile of g_p, and all other variables are as per Eq. 3.

Only trajectories within 500 m of ground level were considered, given that low-altitude air masses are much more likely to show the influence of ground-level sources; however, selection of this 500 m cut-off height was found to have a negligible impact as the identified potential source regions were similar if it was adjusted in a sensitivity analysis by± 300 m~~. The weighted sum was then plotted to depict regions which likely influenced each factor~~, although source regions for a higher cut-off height were expanded over a larger area. The weighted sum was then plotted to depict regions which likely influenced each factor. It should be noted that this approach will highlight the Arctic as a potential source for all factors given that all air masses were initialized at Alert within 500 m of the surface. Thus, interpretation of these plots must consider that they highlight both possible source regions as well as regions the air mass entered on route to Alert. Furthermore, factors with similar peaks will produce similar plots; however it was found that no factor of the selected solution shared more than two dates with peaks above their respective 90th percentile.

3 Results and Discussion

3.1 ~~Selection of~~ Optimal PMF Solution

Positive matrix factorization (PMF) was completed on 49 measurements of 20 analytes in Arctic snow~~. Three metrics were considered~~ (as ~~the basis for this analysis:~~ listed in Table 1). Analysis of snow ~~concentration,~~ measurements as flux per ~~day, and flux per~~ period (i.e., the total deposited mass per area per snowfall ~~(i.e., assuming each sample represented a single snowfall event regardless of the time period over which it occurred, which is known to be true for the majority of samples based on Alert station operator records). Identical PMF analyses were completed for all three metrics, and it~~) was found ~~that the factor profiles identified by all three metrics showed excellent agreement, with Pearson's correlation coefficients above 0.95 for all factors; however, factor contributions varied across the metrics, with correlations as low as 0.35. This is as expected, since the relative variation between analytes does not change with the use of different snow metrics, but the time series should change given that the metrics represent different physical phenomena. The source contributions identified by the flux per snowfall period analysis were~~ to be the most readily interpreted as physically realistic factors. ~~Moreover, this metric showed~~ PMF analyses of the ~~largest correlation between BC~~ snow ~~and atmospheric~~ measurements ~~(Pearson's correlation coefficients of 0.4, 0.3, and 0.5 for BC~~as concentration~~,~~ and flux per day~~, and flux per snowfall period, respectively), implying that the flux per snowfall may in general be more closely related to the change in analyte sources over time while concentration and flux per day may be more intrinsically dependent on changes in deposition processes. Snow flux per snowfall period results will be~~ are presented in the ~~following sections; however, concentration and flux per day results are available in the Table S1 and S2.~~ supplemental S3. Based on the criteria outlined in section 2.4.1, ~~the~~a seven-factor solution was found to be optimal. The seven-factor solution produced one of the largest ~~Q_{rob}~~Q-value improvements with the addition of a factor, an acceptable ~~Q_{rob}/Q_{exp}~~ relative Q value, and good reproducibility. In particular, the seven-factor solution showed a marked improvement in fit and interpretability over solutions with fewer factors. The seven-factor solution reproduced measurements with a Pearson's correlation coefficient above 0.8 for all strong analytes. ~~The four, six, and seven-factor solutions all provided readily interpretable source profiles, but the seven-factor solution was considered the most realistic.~~ Furthermore, a repeat run using 500 seeds showed the seven-factor solution to be consistent and stable. The supplemental section S2 provides additional details on solution selection and the evolution of factor profiles over the completed runs. A brief overview of the results of the four and six-factor solutions is provided in the supplemental, as these solutions also showed merit as realistic apportionments of the data~~.~~

~~Rotations were explored for the selected solution~~, although with ~~FPeak values of -1.5, -1, -0.5, 0.5, 1,~~poorer predicted/measured fit and ~~1.5, though only the -0.5 and -1 runs were found to converge. However, G-space analysis of the base and~~residual error. Potential rotated solutions were considered, but showed no improvement ~~with rotation nor did Q_{rob} values or interpretability of the solution improve; therefore,~~over the unrotated base solution~~ was selected.~~. The final solution statistics ~~were: Q_{rob} = 355, Q_{exp} = 329, Q_{rob}/Q_{exp} = 1.08, stability = 94%, and median predicted/measured correlation = 0.94.~~are summarized in the supplemental section S2.3. The input and model diagnostic parameters for each analyte included in this PMF analysis are provided in Table 1. Only the portions considered as insoluble for metals measured by ICP-MS were included in this analysis (Al, V, Cu, As, Se, Sb, and Pb). Residuals of all analytes were found to be normally distributed, based on PMF5's Kolmogorov-Smirnoff test, with the exception of NO_3^- and V, although both appear visually to be close to a normal distribution.

Table 1: Overview of PMF seven-factor solution input and diagnostic properties.

Analyte	Input Properties			Diagnostic Properties		
	MDL (ppb)	Missing Data	Data Below MDL	Predicted/ Measured Fit	Normalized Residual Mean	Normalized Residual Deviation
Strong Analytes						
BC	0.042	0%	0%	1.00	0.01	0.20
ACE	4.4	0%	4%	0.90	0.08	0.85
FOR	1.2	0%	0%	0.83	0.13	0.77
Cl^-	18	0%	0%	0.96	0.03	0.43
NO_3^-	5.0	0%	4%	0.99	0.01	0.22
SO_4^{2-}	18	0%	0%	0.99	0.01	0.20
Na^+	18	0%	4%	0.99	0.02	0.38
NH_4^+	5.0	0%	2%	0.85	0.07	0.65
K^+	5.0	0%	12%	0.77	0.25	1.11
Mg^{2+}	18	0%	22%	0.95	0.03	0.54
Al	30	8%	27%	0.99	0.00	0.42
V	0.027	8%	10%	0.97	0.09	0.57
As	0.010	8%	0%	0.93	0.09	0.76
Se	0.084	8%	16%	0.99	0.01	0.43
Sb	0.013	8%	0%	0.87	0.17	0.95
Pb	0.16	8%	8%	0.97	0.05	0.67
Weak Analytes						
MSA	1.9	0%	73%	0.70	0.11	0.53
Br^-	5.0	0%	53%	0.46	0.09	0.49
$C_2O_4^{2-}$	18	0%	63%	0.76	0.01	0.18
Cu	0.23	8%	20%	0.49	0.13	0.55

Notes: ACE = acetate; FOR = formate; MSA = methanesulphonate. Predicted/Measured fit presented is Pearson's correlation coefficient. Metals with a charge are those measured by IC, others are insoluble portions measured by ICP-MS.

3.2 Factor Discussion

~~The profiles and contributions of each identified factor are discussed in the following section.~~ The seven PMF factors are described by their composition (Figure 1), contribution over time (Figure 2) and potential areas of influence and/or source regions (Figure 3). Error estimates provided for the percent apportionment of each analyte are the 25th and 75th bootstrap analysis percentiles. The bootstrap analysis correctly mapped over 96% of sub-sampled data for each factor, with the exception of Factor 7 which was correctly mapped for 76% of the bootstrapped runs. Furthermore, sensitivity runs and ~~PCA~~additional analysis ~~all~~(as described in the supplemental) corroborated the presented results. Details on the solution sensitivity and validation analysis are provided in the supplemental.

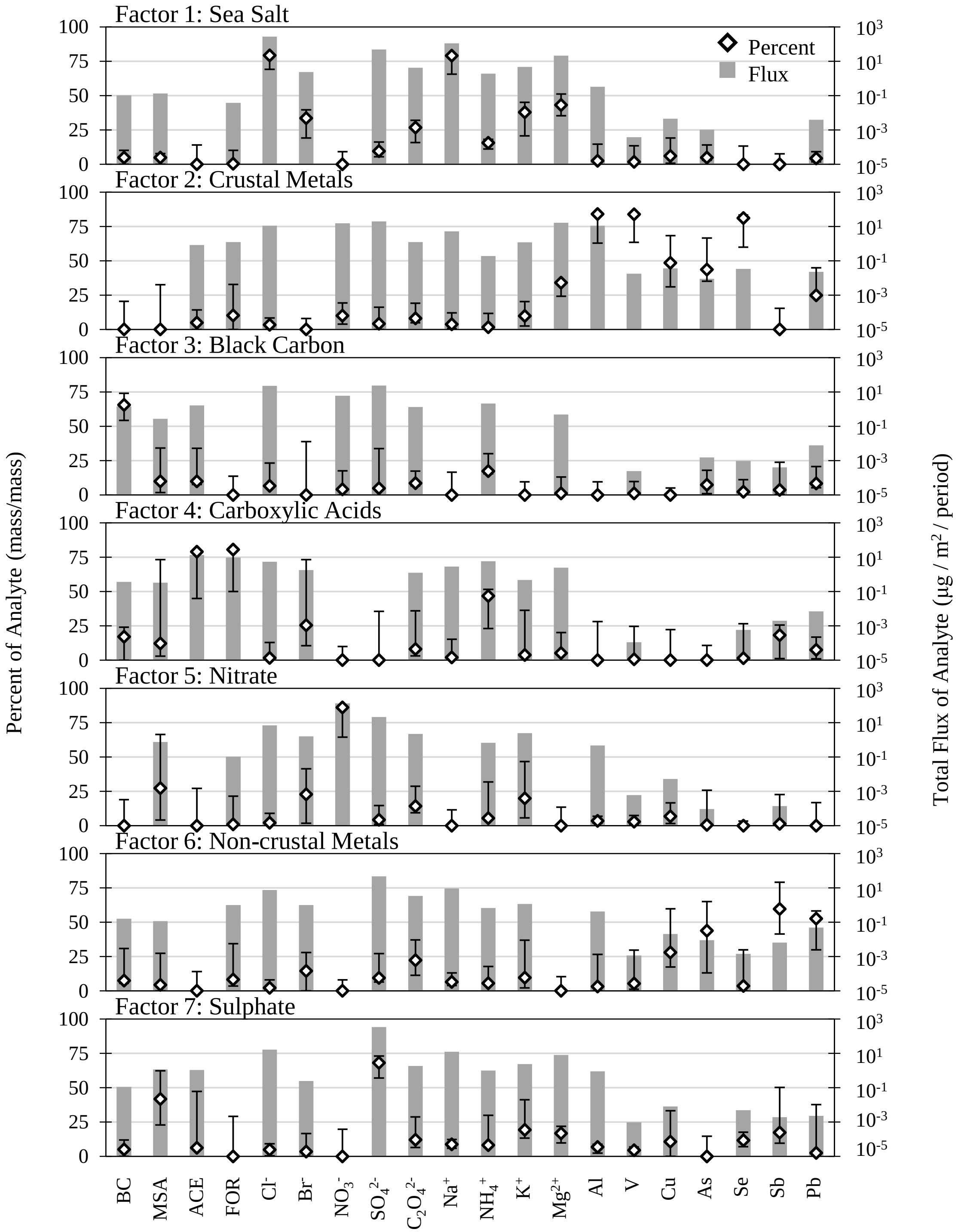


Figure 1: Factor profiles. The loading of each analyte to each factor is provided as the portion of their flux apportioned to that factor as well as the percentage of the analyte's total flux (mass/mass) apportioned to that factor. Error bars on the percentage loading show the 25th and 75th percentiles of the bootstrapping analysis. Flux contributions below 0.00001 $\mu g/m^2$/period are not shown. Metals with a charge are those measured by IC, others are insoluble portions measured by ICP-MS.

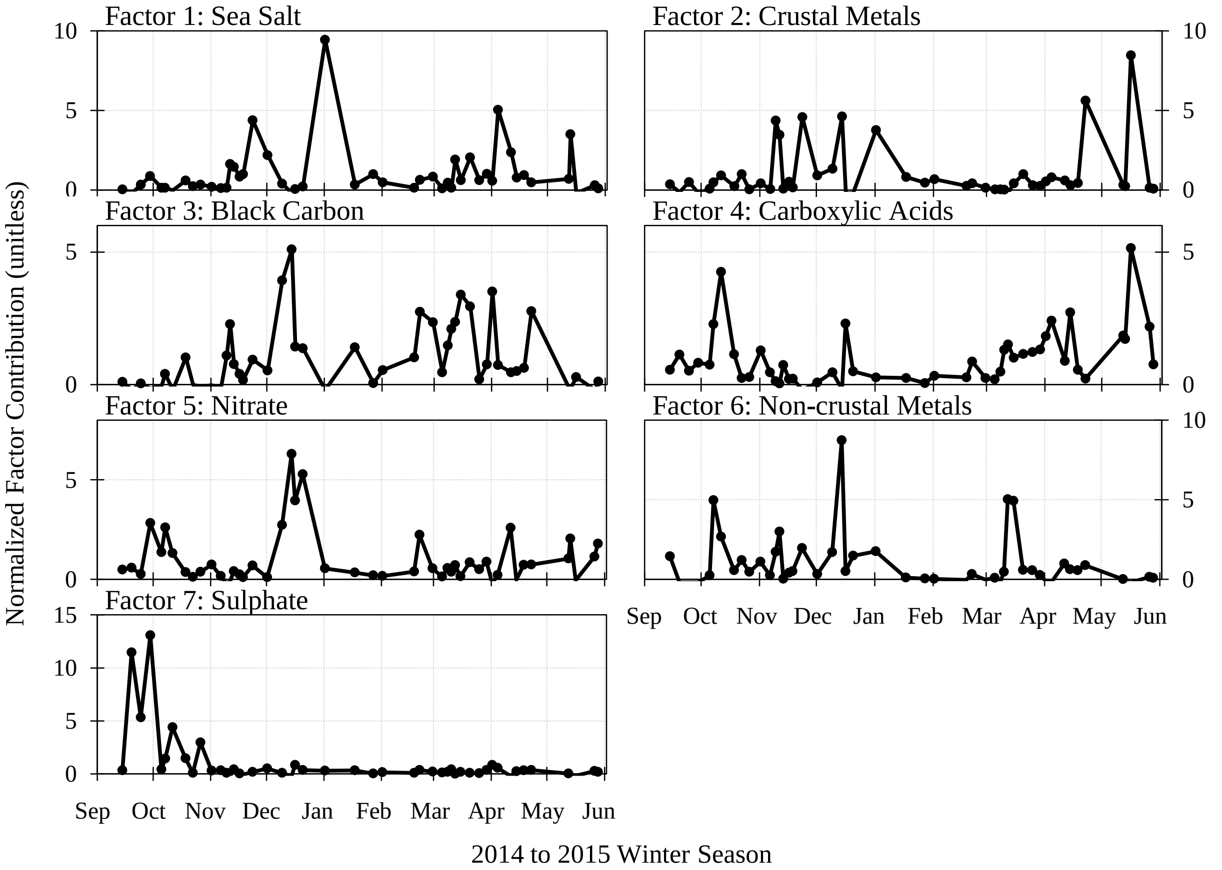


Figure 2: Normalized factor contributions. The unitless contributions describe the relative magnitude of each factor over time such that the average contribution of each factor is one. For example, for the snowfall in early January Factor 1 sea salt had a contribution that was approximately ten times its average contribution over the campaign.

The possible identities of each factor were suggested based on their composition, time series, correlations with non-apportioned analytes (i.e., ~~an analyte which was excluded from the PMF analysis) or with other measured parameters such as meteorology, and source regions.~~ analytes which were not included in the PMF apportionment) or with other measured parameters such as meteorology, and source regions. Table 2 summarizes the dominant analytes associated with each factor and their approximate breakdown of potential influencing regions. A neutralization ratio is also presented for each factor (i.e., [Na$^+$+NH$_4^+$+K$^+$+Mg^{2+}] / [MSA+ACE+FOR+Cl$^-$+Br$^-$+NO$_3^-$+SO$_4^{2-}$+C$_2$O$_4^{2-}$], all as equivalence/m^2/period). Finally non-apportioned analytes and other measured parameters were correlated against the factor contribution time series and notable correlations are included in Table 2 below (Pearson's correlation greater than 0.7 are considered strong, and greater than 0.3 weak; listed in descending order).

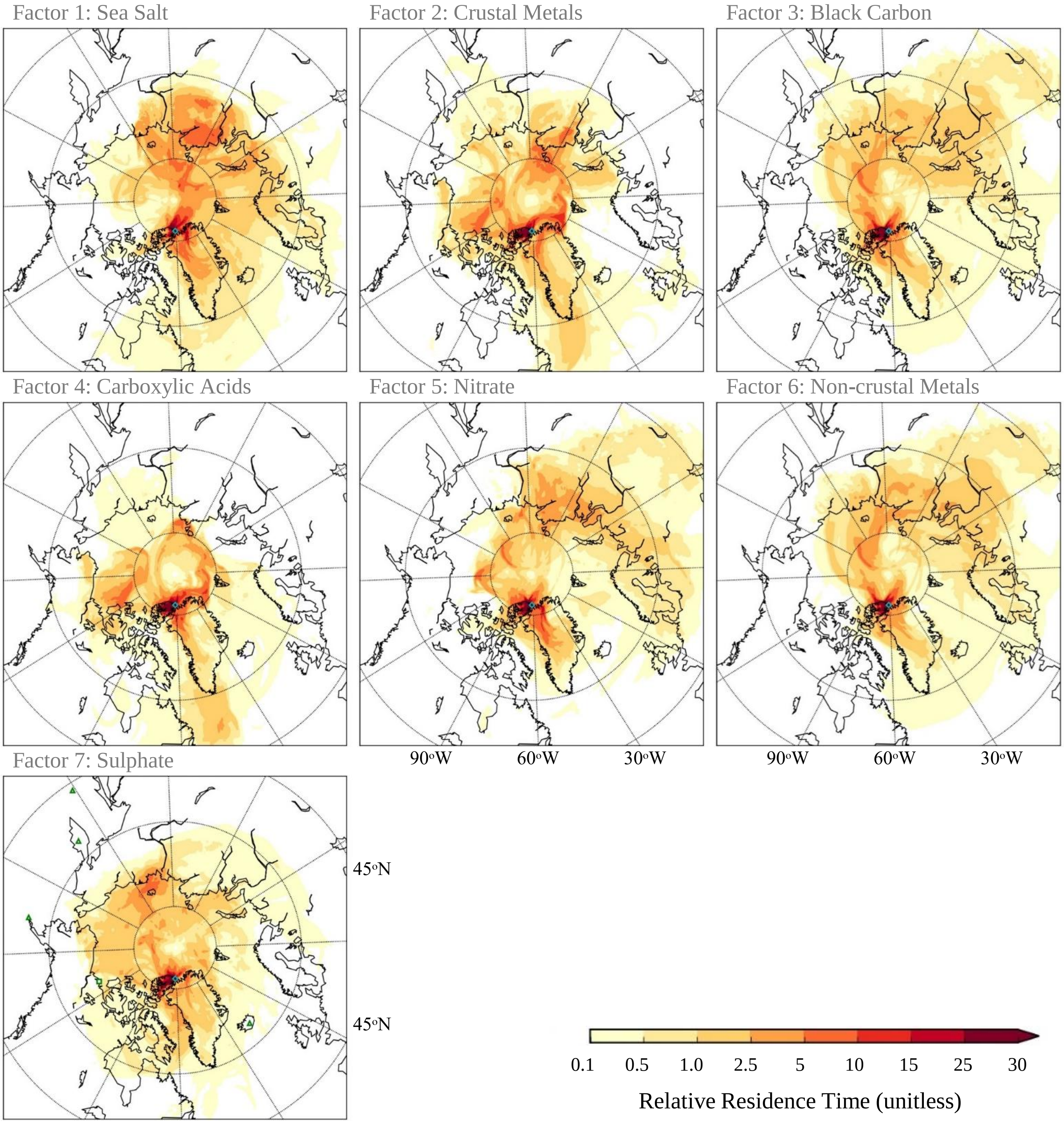


Figure 3: Potential ten-day area of influence/source regions of apportionment factors. Cyan diamonds on plot shows the location of Alert, Nunavut. The Factor 7 sulphate plot depicts active volcanoes as green triangles, and the Smoking Hills as a green square (Hunter, 2007).

Table 2: Overview of factor characteristics.

Factor	Dominant Composition	Source/Influence Regions (% Residence Time)				Neutralization Ratio	Peak Period(s)	Correlated Parameters
		Arctic	North America	Eurasia	Open Ocean			
1. Sea Salt	Na^+, Cl^-	84%	1%	14%	2%	0.79 [0.75-0.84]	episodic	Weak: period length
2. Crustal Metals	Al, V, Se	92%	1%	5%	2%	1.54 [1.17-2.11]	episodic	Strong: Fe, Mn, Co Weak: Ca^{2+}, Ti, basecamp winds
3. Black Carbon	BC	85%	0%	14%	1%	0.12 [0.17-0.38]	winter	Weak: Ti, As (soluble) Anti-corr.: temp.
4. Carboxylic Acids	FOR, ACE	94%	2%	1%	3%	1.02 [0.56-1.24]	fall/ spring	Weak: Ba, basecamp winds, propionate, sunlight
5. Nitrate	NO_3^-	83%	0%	16%	1%	0.04 [0.03-0.19]	episodic	Weak: Ti, H^+, NO_2^-,
6. Non-Crustal Metals	Sb, Pb, As	82%	0%	17%	1%	0.36 [0.30-0.60]	episodic	Weak: Ti, As (soluble)
7. Sulphate	SO_4^{2-}, MSA	91%	3%	6%	1%	0.17 [0.15-0.30]	fall	Strong: NO_2^- Weak: H^+, Ba, Ca^{2+}, temperature, sunlight

Notes: "Open Ocean" is defined as areas of the Atlantic and Pacific below 65 °N. "Arctic" source area includes the northern Pacific/Atlantic Oceans, Arctic Ocean, Canadian high Arctic, and Greenland. Neutralization ratio is described as: optimal solution [25th-75th bootstrapping]. Metals with a charge are those measured by IC, others are insoluble portions measured by ICP-MS unless noted as soluble.

The factor characteristics and possible identifications are discussed in greater detail in the following sections.

3.2.1 Factor 1: ~~Marine~~ Sea Salt

Factor 1 was found to resemble sea salt, primarily based on its composition. The first factor was characterized by high loadings (>75~~%)~~% of total flux mass apportioned to Factor 1) of Na^+ and Cl^- and 30-45% loadings of Br^-, K^+, and Mg^{2+} (Figure 1; Table 2). These ~~compounds are all typical of sea salt, suggesting a marine origin for Factor 1. The composition of Factor 1 was found to be consistent~~ dominant analytes and their relative proportions are consistent with that of sea salt (Pytkowicz and Kester, 1971~~). Comparison of modelled and~~), suggesting a marine origin for Factor 1. The ratios of Cl^- and K^+ to Na^+ in Factor 1 were similar to that expected ~~loadings of marine compounds relative to Na^+ found~~for sea salt with enrichment ratios close to unity~~:~~ of 1.3~~, 1.7, 1.6,~~ and 1.1~~ for Cl^-, SO_4^{2-}, Mg^{2+}, and K^+;~~, respectively~~.~~ (1.3-1.4 and 0.8-1.2 25th-75th percentiles per bootstrapping analysis). The ratios of Mg^{2+} and SO_4^{2-} to Na^+ also resembled that of sea salt, with enrichment ratios of 1.6 and 1.7, respectively (1.5-1.7 and 1.0-1.9 25th-75th percentiles per bootstrapping analysis). Their slight elevation above unity may indicate some enrichment of these ions in the marine aerosol or inclusion of a separate source; however, a Mg^{2+} enhancement of 1.6-1.7 was seen to be consistent among PMF analysis with greater/fewer factors. These enrichment ratios agree well with those measured by Krnavek et al. (2012): 1.33, 1, and 1.4 for Cl^-, K^+, and Mg^{2+}, respectively. The only sea salt ~~compound~~analyte which was notably different from expected marine levels was Br^- with an enrichment ratio of 3.4~~,~~ (2.8-4.2 25th-75th per bootstrapping analysis), which may indicate aerosol enrichment of Br^- relative to Na^+ or may be a result of this analyte's high uncertainty and poor signal-to-noise. ~~Finally, by taking the ratio of equivalence fluxes calculated for all apportioned ions measured by IC, a neutralization ratio of 0.80 was calculated for this factor (i.e., [Na^++NH_4^++K^++Mg^{2+}] / [MSA+ACE+FOR+Cl^-+~~As shown in the supplemental Figure S1, apportioned Br~~$^-$+NO_3^-+SO_4^{2-}+$C_2O_4^{2-}$], all as equivalence/m^2/period),~~$^-$ was underestimated particularly in spring, suggesting that ~~the marine aerosol deposited to the surface was neutral.~~ Br^- spring photo-chemistry (as per that observed by Toom-Sauntry and Barrie, 2002; Pratt et al., 2013) is not well-captured in this PMF analysis.

Factor 1 showed sporadic peaks throughout the campaign, with the largest peak early January (Figure 2). The January peak coincided with a local blizzard, which ~~is consistent with increased sea spray due to windy conditions. Further to this point, the time series of Factor 1 was found to have a slight correlation with local wind speeds, with a Pearson's correlation of 0.3. A dependence on wind speeds might also~~ may indicate ~~a potential frost flower source to this factor, given the~~ local marine sources such as open water, blowing saline snow, or frost flowers. A strong correlation between high winds and salt emissions from fresh sea ice frost flowers ~~which~~ has been ~~observed~~suggested by others (e.g., Xu et al., 2013). ~~No non-apportioned analyte~~ However, Factor 1 also showed ~~significant correlation with Factor 1~~a moderate correlation with collection period length (Pearson's correlation coefficient of 0.47) and the noted January peak was one of the longest collection periods in the campaign This may indicate continuous dry/wet deposition of sea salt to the snow table over time. Weighting the FLEXPART predicted source areas by the Factor 1 peak dates (Figure 3) showed the Eurasian coast of the Arctic Ocean, ~~which remains ice-free for a long portion of the winter, to be a likely source of sea salt to Alert. The Norwegian Sea and northern Atlantic Ocean were also highlighted as potential sources of sea salt to Alert.~~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 contribution the East Siberian Sea, Laptev Sea, and Kara Sea appeared 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.

The marine factor was found to be highly robust over this apportionment analysis. All runs with more than two factors exhibited a resolved Na/Cl-dominated factor, and the composition of this marine factor was found to be maintained across each addition of a new factor with Pearson's correlation coefficients above 0.98. Bootstrapping analysis found little error associated with this factor. Furthermore, similar marine factors have been observed in previous apportionment studies of Arctic snow (Hegg et al., 2009; Hegg et al., 2010) and Arctic aerosol (Sirois and Barrie, 1999; Nguyen et al., 2013). ~~Therefore, Factor 1 was identified as primarily marine in origin based on its agreement with typical sea salt composition. This factor was found to be weakly related to wind speeds, possibly indicating increased salt emissions of frost flowers and sea spray, and largely originating in the ice-free areas of the Arctic Ocean and northern Atlantic.~~

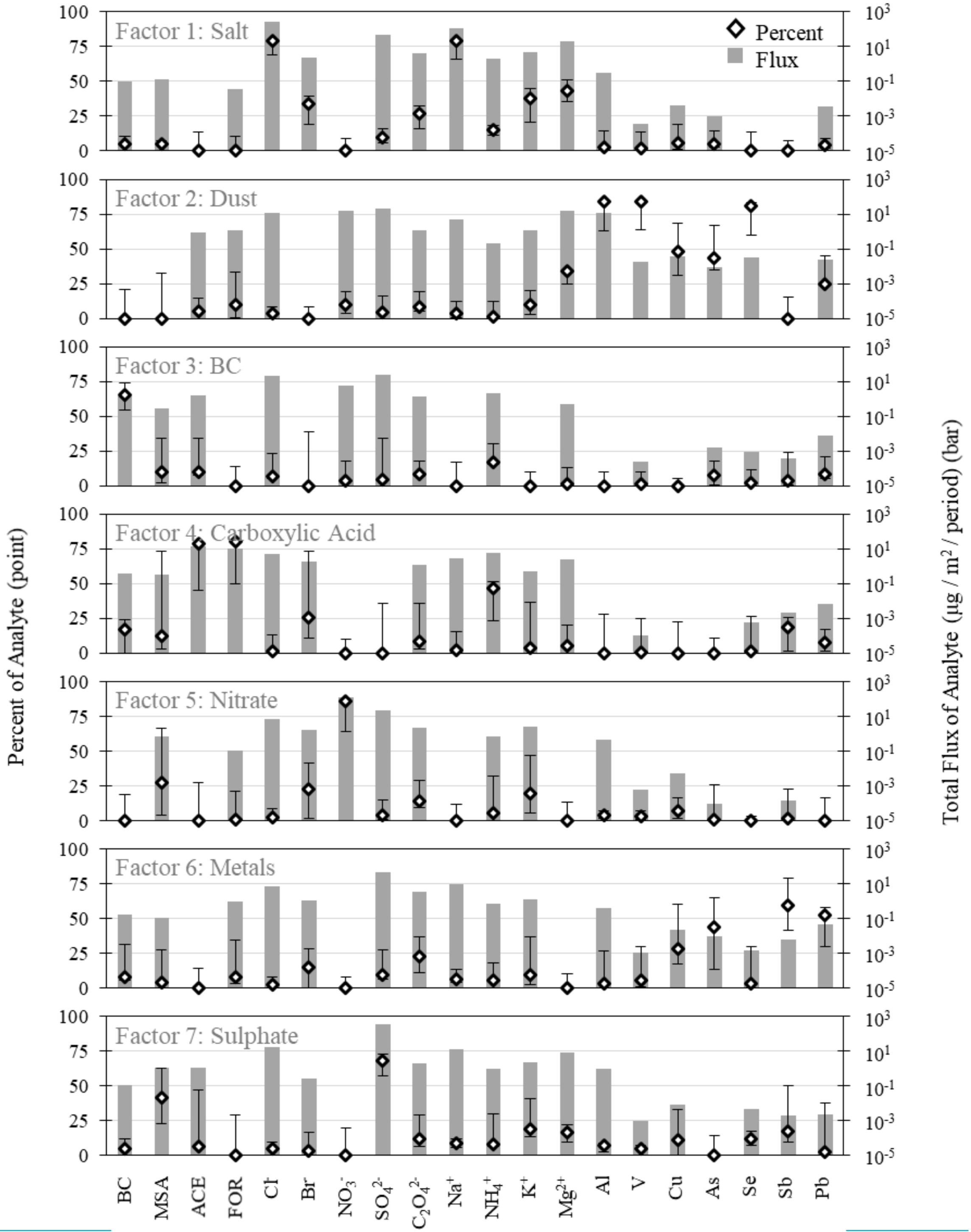
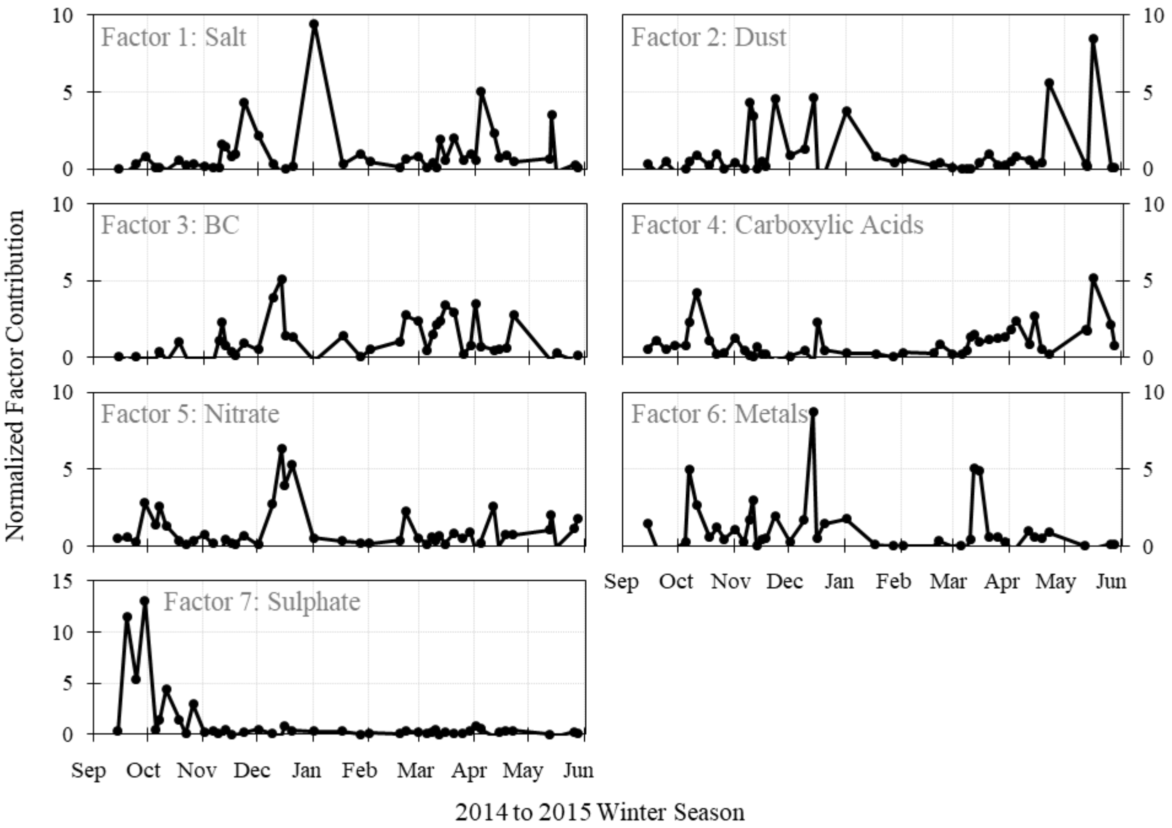


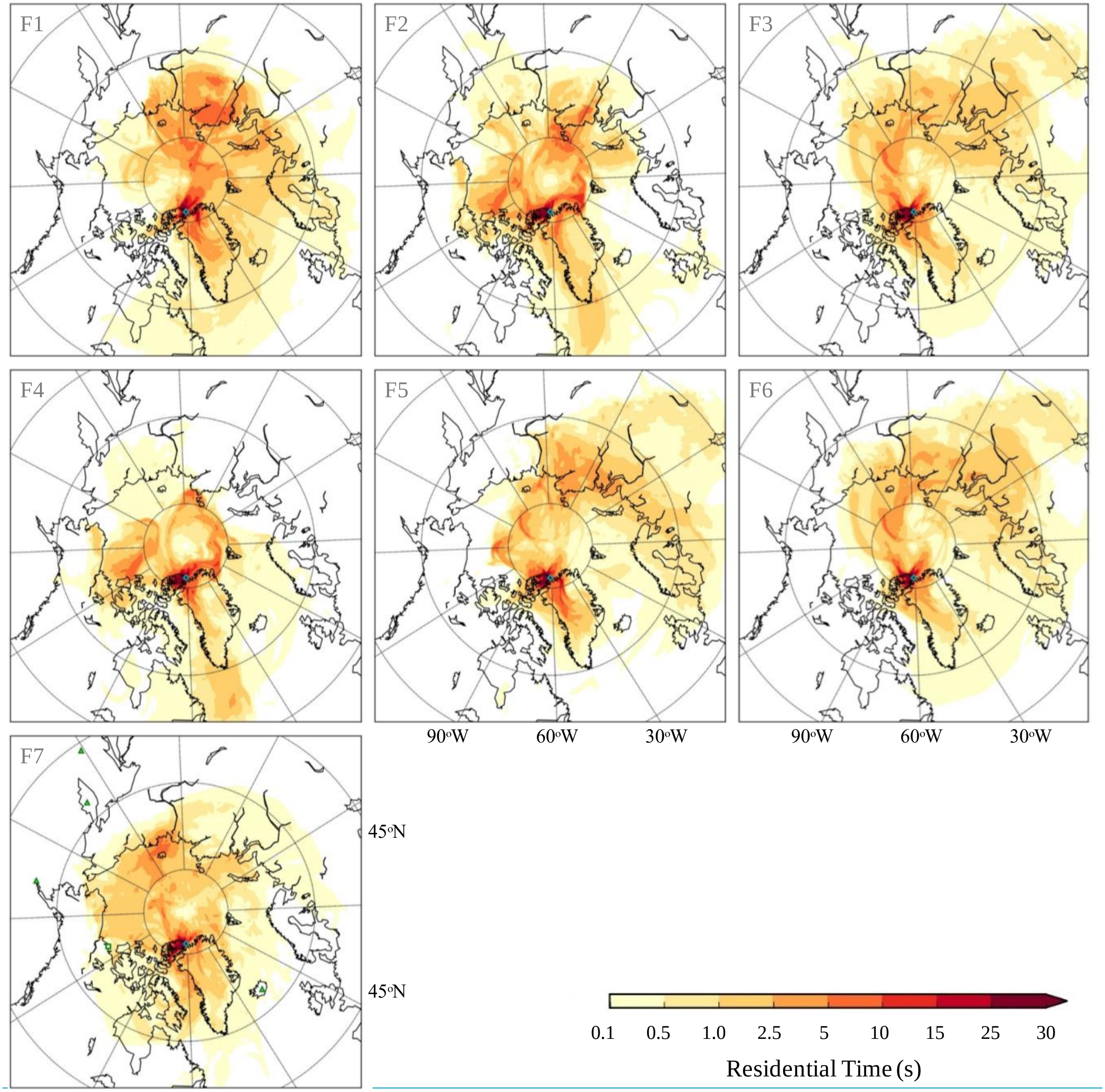
Figure 1: Factor profiles. Error bars show the 25th and 75th percentiles of the bootstrapping analysis. ~~Flux contributions below 0.00001 µg/m^2/period are not shown.~~



~~**Figure 2: Normalized factor contributions.**~~

3.2.2 Factor 2: Crustal Metals

Factor 2 was characterized by elevated levels of Al, V, and Se, all over 80% mass/mass (m/m) loading, and 25-50% loading of Cu, As, Mg^{2+}, and Pb (Figure 1~~). All of these~~; Table 2). These metals suggest a crustal origin for this factor. The composition of dust is far more variable than that of sea salt~~. Thus~~; thus, no single enrichment ratio can be determined for each analyte loaded on to Factor 2~~; however~~. However, the modelled ratios of Al to Mg^{2+}, K^{+}, V, Cu, As, Se, Sb, and Pb all appear realistic when~~ they are~~ compared with a variety of crustal sources, with calculated enrichment ratios in the range of 1 to 15 (Taylor, 1964; Barrie, den Hartog, and Bottenheim, 1989; Masson-Delmotte et al., 2013). Specifically, the modelled ratio of As/Al (0.00081 m/m) was seen to be closer to that of local soils (0.00013) (Barrie, den Hartog, and Bottenheim, 1989) than the global typical composition (0.00002) (Taylor, 1964; Masson-Delmotte et al., 2013) with enrichment ratios of 6 and 37, respectively~~.~~ (6.3-9.5 and 37-58 25th-75th percentiles per bootstrapping analysis). The composition of ~~the Crustal Metals~~ Factor 2, crustal metals, suggested an alkaline aerosol with a neutralization ratio of 1.5, calculated as described in section 3.2~~.1~~.



~~Figure 3: Potential source regions of apportionment factors (F1 to F7).~~Factor 2 ~~Cyan diamonds on plot shows the location of Alert, Nunavut.~~ ~~Factor 7 plot depicts active volcanoes as green triangles, and the Smoking Hills as a green square (Hunter, 2007).~~

~~The Crustal Metals Factor~~ showed sporadic peaks over the campaign but primarily from November to February and after April. This time series showed good agreement with non-apportioned metals typically considered to be dominated by crustal origins: insoluble Fe, Mn, Co, Tl, and Ca. The time series of this factor also showed slight correlations with winds from the direction of the base camp and winds speeds, with Pearson's correlations of 0.39 and 0.26, respectively. This, along with the calculated As/Al ratio, suggest that this crustal factor may be dominated by local soil and dust, likely from cleared or paved areas at the Alert base camp. The potential source regions calculated from FLEXPART results for this factor are shown in Figure 3. Arctic areas dominate the identified potential source region, again suggesting local soils were a major contributor to this factor; however, potential long-range sources of northern Asia, North America and Atlantic Ocean were also identified. A primarily local dust source is supported by the findings of Zwaaftink et al. (2016), which showed that surface dust loads within the high Arctic are typically dominated by Arctic sources with an annual average contribution of ~~78% by concentration or~~ 70% ~~by deposition~~deposited mass from sources above 60 °N.

A factor dominated by crustal metals was consistently resolved among the completed apportionment runs. This factor maintained a fairly similar composition across all numbers of factors, with Pearson's correlation coefficients above 0.97. However, metals traditionally considered to be associated with industrial activities, such as Pb, Cu, As, and Sb, were observed to gradually split from this factor with the addition of new factors. The seven-factor solution for this factor showed low levels of error according to the bootstrapping analysis. Similar factors have been observed in previous atmospheric apportionment studies (e.g., Sirois and Barrie, 1999; Nguyen et al., 2013) but typically were not seen to account for such a large percentage of these metals, i.e., with loadings of 25-60% m/m for major crustal analytes. This might suggest that a separate source was missed by this study, though this seems unlikely given the consistency of the observed factor. Sirois and Barrie (1999) found the crustal signature at Alert to be dominated by local sources during the fall and long-range transport in the late spring to summer. This supports a single local source for this study ~~of~~focussed on the winter season, while studies of the full year may have split crustal analytes among various long-range transport sources. However, the April-May peak in the crustal factor observed in this study coincides with Sirois and Barrie's (1999) peak considered to be dominated by long-range dust transport. ~~Based on the loading of crustal metals, Factor 2 was identified as a crustal source. The composition of this factor resembled that of local Alert soil and the correlation with base camp winds and FLEXPART results support a local origin to this factor. However, previous studies have shown mixed agreement on the dominance of local crustal sources within the Arctic over dust transported from lower latitudes.~~

3.2.3 Factor 3: Black Carbon

The third factor was characterized by a high loading of BC, 66% m/m of the total BC, ~~with~~ 17% m/m loading of NH_4^+, and all other analyte loads below ~~20~~10% (Figure 1). BC is a combustion product from both fossil fuel and biomass burning. While NH_4^+ is more commonly associated with agricultural emissions, it can also be produced by biomass burning, vehicle emissions, and some industrial activities (Behera et al., 2013). Most conspicuous in the composition of Factor 3 was the absence of K^+, considered to be a tracer of biomass burning which can be a significant source of BC. This separation of BC and K^+-rich factors was persistent for all PMF solutions with four or greater factors. Furthermore, the ratios of SO_4^{2-} and NO_3^- to BC were much higher than would be expected for biomass burning with enrichment ratios above ten (Turn et al., 1997; Hays et al., 2005; Saarikoski et al., 2007; McMeeking et al., 2009~~). Factor 3 also exhibited a moderate NH_4^+~~; May et al., 2014); the relative loading of ~~17%. While NH$_4^+$ is more commonly associated with agricultural emissions, it can also be produced by~~SO$_4^{2-}$ compared to NH$_4^+$ and NO$_3^-$ was also higher than expected for biomass burning~~, vehicle emissions, and some industrial activities (Behera~~ (Liu et al., ~~2013~~2017). This factor also showed an acidic signature with a neutralization ratio of 0.12~~, which suggest an industrial rather than biomass burning source.~~

~~The Black Carbon.~~ Factor 3, BC, showed an enhanced contribution over the Arctic Haze season, November through April (Figure 2). The time series of this factor did not show a ~~significant~~strong correlation with any non-apportioned analyte; however, it did show weak correlations with insoluble Ti and ~~Tl and inverse correlations with temperature and humidity. Also~~V, and soluble As. The observed winter enhancement of this factor did not suggest a significant contribution from forest fires which are more prevalent in warmer months. Furthermore, the peaks in this factor did not coincide with dates of known northern hemisphere forest fire activity (as per fire records of NASA Global Fire Maps, retrieved May 2016 from https://lance.modaps.eosdis.nasa.gov). ~~Further to this point, the observed winter peak of this factor did not suggest any significant contribution from forest fires which are more prevalent in warmer months. Weighting of FLEXPART results by peak periods for Factor 3 indicated that Eurasia was a probable source of this factor (Figure 2), especially northern Russia and some portions of central southern Russia. These source regions correspond with known flaring and industrial BC sources (in the vicinity of the Ob and Pechora rivers and the Taymyrsky Dolgano-Nenetsky District, respectively) (Huang et al., 2015).~~Thus, the composition and time series of Factor 3, BC, suggested a predominantly anthropogenic combustion source with little contribution from biomass burning. A BC-dominated factor was resolved for all runs with four or more factors, and its composition remained consistent with Pearson's correlation coefficients of 0.95 or greater. Thus, the practically unique origin of BC was fairly robust through this analysis. ~~Furthermore, the loading of non-sea salt (NSS) K$^+$ onto all resolved BC-dominated factors was below 12%, suggesting that a primarily biomass burning origin to BC was unlikely. Based on the elevated SO$_4^{2-}$ levels, the mid-winter peaks, and the Eurasian source region, Factor 3 appears to be predominantly the product of anthropogenic fossil fuel burning, though likely contains a mixture of Eurasian sources: industrial, urban, residential burning, and other minor contributors.~~

There ~~has~~have been ~~considerable disagreement among previous~~many studies ~~on~~exploring the ~~dominant~~sources of Arctic BC, though primarily focussed on aerosol. The relative importance of fossil fuel combustion and biomass burning differs between studies, likely indicating a strong dependence on location (especially high vs low Arctic), season, or differences in source ~~of BC~~ breakdown year-to-year (e.g., McConnell et al., 2007; Doherty et al., 2010; Dou et al., 2012; Law et al., 2014). A recent study by Xu et al. (2017) analysing airborne measurement from a similar time period as this study found about 90% of BC to likely be anthropogenic in source, primarily from Eurasia, supporting the ~~Arctic.~~assessment above. Several modelling studies have suggested that combined anthropogenic sources ~~(fossil fuel and biofuel burning)~~ account for ~~75~~65-96% m/m of BC in Arctic snow, especially elevated over the winter months with spring and summer proportions dependent on the frequency of forest fires of that year (Flanner et al., 2007; Skeie et al., 2011; Wang et al., ~~2011; Xu et al., 2017~~2011; Sharma et al., 2013; Breider et al., 2014; Xu et al., 2017).~~). A recent study by Xu et al. (2017) analysing airborne measurement from a similar time period as this study found about 90% of BC to likely be anthropogenic in source, primarily from Eurasia.~~ In particular, modelling studies have shown winter Arctic BC to be dominated by flaring and other mixed industry emissions, with less impact from anthropogenic biomass ~~(often termed biofuel)~~ burning (Flanner et al., 2007; Stohl et al., 2013). ~~Similarly, studies~~ Studies of Arctic snow/aerosol composition have suggested that over 85% of BC is from the combustion of fossil fuels year-round, based on radiocarbon analysis and measured ratios with biomass burning tracers (e.g., Slater et al., 2002; Yttri et al., 2011; Yttri et al., 2014~~). In contrast, previous apportionment~~ ; Barret et al., 2015). Hegg et al. (2009 and 2010) completed snow PMF apportionment analyses on spatially-defined samples. Unlike the majority of studies discussed above, these apportionment studies of Arctic spring snowpack ~~have~~ attributed over 90% of BC to biomass burning origins ~~(Hegg et al., 2009;~~. The Hegg et al~~., 2010). These contradicting snow BC apportionment findings may be the result of spatial and temporal differences between this~~. (2009 and ~~previous~~2010) studies~~, specifically the stronger focus on low Arctic locations and spring sampling within these previous studies. Although high Arctic winter snow samples were sparse in previous apportionment studies, the few available~~ showed ~~an enhanced fossil fuel signature, though over 30% of BC at these sites was still attributed~~the variability in BC sources to snow by location and season; however, in nearly all cases, including aged winter snow, pollution sources were found to be small contributors relative to biomass burning ~~(Hegg et al., 2010).~~. This ~~smaller discrepancy cannot be satisfactorily explained by the annual variability in biomass burning intensity, as~~may indicate a significant fluctuation in BC sources between years; however, both ~~study periods~~the 2014/15 season and the years of interest in the Hegg et al. studies (2009 and 2010) were found to represent fairly typical years in Northern hemisphere biomass burning emissions (Global Fire Emissions Database, version 4.1, retrieved July 2016 from http://www.globalfiredata.org). ~~Table 2 summarizes the apportionment of BC by the studies discussed above. Overall, the loading of winter BC onto one major source with a largely fossil fuel combustion origin is generally in agreement with previous modelling and snow composition studies, though unexpectedly different from some previous snow apportionment studies.~~ Thus, the findings of this study stress the variability in BC sources to Arctic snow and the importance of further measurements to better classify the main contributions.

~~**Table 2: Overview of BC apportionment studies.**~~

~~Analysis~~	~~Study~~	~~Description~~	~~BC Apportionment (%)~~		
			~~FF~~	~~BF~~	~~BB~~
~~Co-Variance~~	~~This Work~~	~~Temporally-refined snow PMF~~	~~73%~~	↔	~~17%~~
	~~Hegg et al. 2009~~	~~Spatially-refined snow PMF~~	~~7%~~	→	~~93%~~
	~~Hegg et al. 2010~~	~~Spatially-refined snow PMF~~	~~6%~~	→	~~90%~~
~~Model~~	~~Flanner et al. 2007~~	~~SNICAR + general circulation model~~	~~60-70%~~	~~20%~~	~~10-20%~~
	~~Skeie et al. 2011~~	~~Oslo CTM2 model~~	~~85-95%~~	←	~~5-15%~~
	~~Wang et al. 2011~~	~~GEOS-Chem CTM~~	~~45-60%~~	~~15-35%~~	~~10-40%~~
	~~Xu et al. 2017~~	~~GEOS-Chem (global, spring)~~	~~90%~~	↔	~~10%~~
~~Composition~~	~~Slater et al. 2002~~	~~Radiocarbon~~	~~60-100%~~	→	~~0-40%~~

	~~Yttri et al. 2011~~	~~Radiocarbon~~	~~>95%~~	~~→~~	~~<5%~~
	~~Yttri et al. 2014~~	~~Levoglucosan ratio~~	~~85-95%~~	~~→~~	~~5-15%~~

~~**Notes:** **FF = Fossil fuel, BF = Biofuel, BB = Biomass burning. Arrows indicate when BF has been grouped in with FF and/or BB.**~~

Weighting of the FLEXPART results by the peak periods for Factor 3 indicated that central Eurasia was a probable source of this factor, especially northern Russia and some portions of central southern Russia (Figure 3). Russian industrial activities are known to be a significant source of BC; in particular, some studies have estimated about 70% of Russian BC emissions are related to flaring and transportation (Evans et al., 2017). These source regions correspond with known flaring and industrial BC sources (in the vicinity of the Ob and Pechora rivers and the Taymyrsky Dolgano-Nenetsky District, respectively) (Huang et al., 2015; Winiger et al., 2017). A winter central Eurasian source of BC was also identified by Xu et al. (2017), specifically flaring in western Siberia. However, this central Asian source was found to be a smaller contributor of total Arctic BC than eastern Asia. Similarly, Hirdman et al. (2010) and Stohl et al. (2007) also identified a primarily northeastern Eurasian source to Arctic BC in the winter/late spring. The lack of a distinct eastern Asian source for Factor 3, BC, may indicate that the ten-day trajectory analysis was not long enough to fully capture this influence.

3.2.4 Factor 4: Carboxylic Acids

Factor 4 was characterized by high loadings, 79-80~~%,~~% m/m, of acetate (ACE) and formate (FOR); moderate loadings, 25-50%, of NH$_4^+$ and Br$^-$; and lower loadings, 10-20%, of Sb, BC, and MSA (Figure 1; Table 2). The loadings of Br$^-$ and MSA on this factor were highly variable, as shown by the bootstrap results in Figure 1; however, both of these analytes had high associated uncertainty. The composition of this factor suggested a neutral aerosol with a neutralization ratio of 1.02. Factor 4 exhibited peaks in October and May (Figure 2) and was seen to moderately correlate with propionate, hours of sunlight, and base camp winds, with Pearson's correlation coefficients of 0.4-0.5. Weighted FLEXPART results indicated ~~a~~ local, North American, and~~/or~~ Atlantic Ocean ~~source~~areas of potential influence for this factor~~.~~ (Figure 3). A variety of potential source may have contributed to this factor but the available evidence does not allow a robust identification. Possible contributors hypothesized in other studies of arctic carboxylic acids are discussed below including biomass burning, atmospheric or snow photochemical processing, and ocean microlayer emissions. However, some studies have postulated the existence of a yet unidentified source of high-latitude carboxylic acids (e.g., Paulot et al., 2011) which may be reflected in Factor 4. A similar high carboxylic acid factor was resolved for runs with six or greater factors and maintained its composition with Pearson's correlation coefficients of over 0.96; however, the loading of BC and K$^+$ onto this carboxylic acid factor was much more variable over the additional runs.

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). The ratio of BC and K$^+$ apportioned to this factor was similar to that of a biomass burning plume, particularly ~~to~~ the high K$^+$ proportion typical of herbaceous burning (Turn et al., 1997; Saarikoski et al., 2007; McMeeking et al., 2009~~); however~~; May et al., 2014). However, both BC and K$^+$ loading showed significant uncertainty. The loadings of formate, acetate, Cl^-, Br^-, $C_2O_4^{2-}$, and NH_4^+ appeared to be higher than expected for biomass burning emissions~~:~~; the ratio of these analytes to BC were enriched by a factor of 3 to ~~40~~75 relative to typical ratios of biomass burning emissions, based on a review of measured herbaceous and woody emissions (Turn et al., 1997; Andreae and Merlet, 2001; Hays et al., 2005; Saarikoski et al., 2007; McMeeking et al., 2009; May et al., 2014). The observed enrichment ratios of this factor above typical biomass burning plumes could be explained by atmospheric processing, for example, the cloud processing suggested by Legrand and de Angelis (1995). Alternatively, gas-phase partitioning and the subsequently enhanced scavenging observed in a previous study of this data (Macdonald et al., 2017) may have led to increased levels of some co-emitted chemical species relative to BC. The fall and spring peak of Factor 4 may support a biomass burning identification, as burning events are more typical in warmer seasons, specifically a North American source as suggested by the FLEXPART analysis.

Previous studies have also suggested a photochemical processing source of these carboxylic acids in the Arctic. Dibb and Arsenault (2002) found elevated levels of formic and acetic acid in the pore space of deposited Arctic snow and hypothesized oxidation of carbonyls and alkenes within the snowpack as a likely source. The prevalence of the factor in the fall and spring, before polar sunset and after polar sunrise, would support a photochemical source. Furthermore, summertime measurements of Arctic atmospheric samples by Mungall et al. (2017) also showed high levels of formic and acetic acid~~. This study~~ and hypothesized an oceanic microlayer photochemical source. Again, the temporal trend of Factor 4 as well as the Atlantic Ocean source location would support this possibility. An atmospheric budget analysis by Paulot et al. (2011) identified a significant missing source of high-latitude formic and acetic acid. Factor 4 of this study could represent a combination of the suggested sources above, or a missing source which is as yet unidentified.

3.2.5 Factor 5: Nitrate

The fifth factor was characterized by high NO_3^-, 86% m/m loading (Figure 1). This factor was also seen to have moderate loadings of MSA and Br^-, 20-30%, but with a larger degree of uncertainty. The atmospheric chemistry of NO_3^- is complex, involving a variety of sources, formation mechanisms, and destruction mechanisms; in particular, snow can act as both a sink and a source of atmospheric nitrogen oxides, further complicating the local NO_3^- cycle (Beine et al., 2002; Ianniello et al., 2002; Morin et al., 2008; Fibiger et al., 2016). Furthermore, the complex processing of NO_3^- was demonstrated in the earlier deposition analysis of this data which suggested that gas-phase deposition was a dominant mechanism of NO_3^- transport ~~into~~to snow (Macdonald et al., 2017). Thus, the loading of NO_3^- onto a separate factor may be a reflection of its unique atmospheric processing. Comparison of simultaneous snow and atmospheric measurements over this campaign, as described in Macdonald et al. (2017), showed NO_3^- to have a higher effective deposition velocity than BC or SO_4^{2-}. This supports external mixing of these compounds in the atmosphere and thus their assignment to separate source factors. This NO_3^--loaded factor was resolved for simulations with six or greater factors, prior to which this factor appears to be combined with the carboxylic acid factor. In addition, a similar unique NO_3^- factor was also observed in previous snow and atmospheric apportionment studies (Sirois and Barrie, 1999; Hegg et al., 2009; Hegg et al., 2010).

Factor 5 showed a variable contribution throughout the campaign but especially elevated in December. This factor was not found to correlate significantly with any non-apportioned analyte or meteorological parameter; however, Factor 5 did weakly correlate with nitrite (NO_2^-) and H^+ with Pearson's correlation coefficients of 0.35 and 0.46, respectively. This correlation with H^+ is in agreement with this factor's low neutralization ratio of 0.04. The low fall/spring levels of this factor may reflect the loss of NO_3^- from snow through photolysis driven by the sunlight availability after polar sunrise (Morin et al., 2008; Fibiger et al., 2016). The highest NO_3^- levels were observed when photolysis ~~is~~was inhibited during the polar sunset from mid-October to late-February. The movement of NO_3^- accumulated in the snow to atmosphere during the spring is supported by the broad peak in atmospheric NO_3^- observed via Hi-Vol filters from February to the end of the atmospheric sampling in mid-May. February to June, 2015, was also characterized by a "bromide explosion", observed as a broad peak in snow and atmospheric Br^-~~.~~$^-$ (Macdonald et al., 2017). It is possible that this offered a different formation pathway for NO_3^- over this period via the reaction of NO_2 and BrO (Morin et al., 2008). The mid-winter peak in this factor may be linked to NO_3^- formation via ~~NO_3-radical chemistry~~N_2O_5 hydrolysis in the aerosol phase, which is considered to dominate Arctic NO_3^- chemistry during the night (Morin et al., 2008).

Potential source areas of this factor, largely driven by the December peak, are shown in Figure ~~2~~3. This plot was found to be similar to that of Factor 3, primarily northern Eurasia, though with a possible stronger dependence on northern Europe. Thus, the NO_3^- precursors to this factor may be largely anthropogenic in origin. Additionally, this factor appears to coincide with increased transport over the ice-free ~~Norwegian Sea and northern Atlantic.~~ open water. This transport pathway might explain the presence of MSA, typically considered an indicator of marine biogenic activity within warmer ice-free water bodies (Li et al., 1993; Ye et al., 2015).

3.2.6 Factor 6: Non-Crustal Metals

Factor 6 showed a high loading of Sb, Pb, and As, 40-60% m/m, and moderate Cu loading, 28%, as shown in Figure 1. These metals are frequently associated with industrial emissions, particularly high-temperature activities such as fossil fuel combustion and smelting (Berg, Røyset, and Steinnes, 1994; Laing et al., 2014). Although total Se and V loadings to this factor are low, the non-crustal loading of these metals (i.e., percentage of total excluding that which is loaded on Factor 2) are 20-30%. This factor also contains 10% of non-sea salt SO_4^{2-}. These constituents also point towards an industrial source (Berg, Røyset, and Steinnes, 1994; Laing et al., 2014). A neutralization ratio of 0.37 for this factor suggested an acidic aerosol. Factor 6 exhibited major peaks in October, December, and March and was found to be associated with a Eurasian source (Figure 2 and 3). Although several of the non-apportioned metals had limited measurements above MDL, a possible correlation was observed between Factor 6 and insoluble Ti, Cr, and Tl, and soluble As, Pb, Cr, and Cd. These metals are often considered to be primarily industrial in origin (Berg, Røyset, and Steinnes, 1994; Laing et al., 2014). The similarity in the FLEXPART potential source maps between Factor 3 ~~(~~BC~~)~~ and Factor 6 may support their mutual designation as anthropogenic-related.

Factors 6 and 7 were resolved separately only for solutions with seven or more factors. With the addition of a ninth factor, the non-crustal metals factor was further split into a factor dominated by As and Pb and a second factor dominated by Sb. This may represent the resolution of different industrial sources; however, the addition of these factors was not found to greatly improve the overall solution fit. Factors dominated by non-crustal metals, specifically Pb and As, have been observed in previous atmospheric apportionment studies (Sirois and Barrie, 1999; Nguyen et al., 2013) but not as clearly in existing snow apportionment studies (Hegg et al., 2009; Hegg et al., 2010).

3.2.7 Factor 7: Sulphate

Factor 7 was characterized by SO_4^{2-} and MSA, with loadings of 68% and 42% m/m, respectively (Figure 1). MSA is considered to be a tracer for biogenic marine activity; however, the ratio of MSA/SO_4^{2-} observed in Factor 7, 0.003, is far below that typically seen for marine biogenic emissions, 0.05-0.20 (Li et al., 1993). The portion of SO_4^{2-} in this factor related to marine biogenic emissions was estimated at about 2-7%, assuming a typical MSA/marine-SO_4^{2-} ratio and similar scavenging of MSA and marine SO_4^{2-}. Thus, an additional source of SO_4^{2-} to this factor was suggested. Sulphate is typically an indicator of anthropogenic activities; however, the potential source regions identified for Factor 7 in Figure 3 are largely confined to the Arctic where anthropogenic sources are minimal. The source region identified is only a ten-day back trajectory, so it is possible that the area of influence would extend farther south if longer trajectories were considered. However, given that 91% of the ten-day FLEXPART area is within 65 °N, a northern and likely natural source seems likely. Furthermore, BC and NO_3^-, typical indicators of industrial activity, both showed low loadings (<6% m/m) onto Factor 7, again suggesting this factor is not anthropogenic in origin. The loading of SO_4^{2-} onto Factor 3 BC and Factor 6 non-crustal metals are more consistent with anthropogenic sources.

Aside from anthropogenic and marine sources, volcanic activity can be a significant source of atmospheric SO_4^{2-}. Volcanic emissions are characterized by high levels of sulphur dioxide (SO_2, an oxidation precursor of SO_4^{2-}), acidic compounds, and a variety of metals (AMAP, 2006). A volcanic source would be consistent with the observed low levels of BC and NO_3^- associated with Factor 7~~Thus, an additional source of SO_4^{2-} to this factor was suggested.~~. Significant loadings of non-crustal Se and V (62% and 28% m/m, respectively), correlation with H^+ and Ba, and an acidic neutralization ratio also support a potential volcanic source for Factor 7 (Key and Hoggan, 1953; Rahn, 1971; Berg, Røyset, and Steinnes, 1994; AMAP, 2006; Laing et al., 2014). Several volcanoes within the near Arctic were known to be active over the 2014-15 season: Bárðarbunga, Iceland; Shishaldin, Aleutian Islands; Sheveluch, Bezymianny, and Zhupanovsky, Kamchatka Peninsula; and Chirpoi, Kuril Islands (Global Volcanism Program, retrieved March 2016 from http://volcano.si.edu/). The Smoking Hills, naturally combusting coal and oil shale deposits on the northern coast of the Northwest Territories, Canada, at Cape Bathurst, 69.5 °N, 126.2 °W, are also located near the identified source region of Factor 7 (Freedman et al., 1990; AMAP, 2006); however, it is expected that the contribution from these hill would be minimal. Factor 7 showed a distinct maximum in September/October and a low contribution throughout the remainder of the campaign. This corresponds with volcanic activity at the Bárðarbunga volcano in Iceland as observed by others (Icelandic Met Office via Global Volcanism Program, retrieved March 2016 from http://volcano.si.edu/). Comparison of these snow measurements to previous seasonal snow measurement campaigns (e.g., Davidson et al. 1993; Toom-Sauntry and Barrie, 2002) showed this fall peak in SO_4^{2-} snow concentration and flux to be unusual. This further supports a non-seasonal event such as a volcanic eruption as a major contributor to Factor 7, sulphate. These volcanic sources are shown on the source region plot for Factor 7 sulphate as well as the smoking hills for context (Figure 3). Although none of these locations appear to have high associated residence times within the ten-day back trajectory analysis, they appear closer to the identified source regions than major industrial activities farther south. Given the heat and velocity of a volcanic emission, the near-surface restriction applied to the FLEXPART trajectories to identify likely source regions may not be appropriate for Factor 7. Supplemental section S2.2 provides potential source/influence region plots for peak fall periods associated with Factor 7 for a larger range of source altitudes: 0 to 10 km above ground level. These plots do show potential influence from Bárðarbunga in Iceland~~Volcanic emissions are characterized by high levels of sulphur dioxide (SO$_2$, an oxidation precursor of SO$_4^{2-}$), acidic compounds, and a variety of metals (AMAP, 2006). A volcanic source would be consistent with the observed low levels of BC and NO$_3^-$ associated with Factor 7, which do not suggest an industrial source. In addition, Factor 7 contained 62% of the non-crustal Se signature and 28% of non-crustal V. Non-crustal Se is typically considered to be a tracer of coal combustion and V a tracer of oil combustion (Laing et al., 2014). The Smoking Hills are located on the northern coast of the Northwest Territories, Canada, at Cape Bathurst, 69.5 °N, 126.2 °W. These hills are a natural phenomenon whereby coal and oil shale deposits within the hills have been combusting for centuries, continuously emitting sulphur and metal aerosols (Freedman et al., 1990; AMAP, 2006). Thus, Factor 7 appeared to be related to natural regional SO$_4^{2-}$ sources: marine biogenic activity and volcanic and/or Smoking Hills activity. The portion of SO$_4^{2-}$ in this factor related to marine biogenic emissions was estimated at about 2-7%, assuming a typical MSA/marine-SO$_4^{2-}$ ratio and similar scavenging of MSA and marine SO$_4^{2-}$. Also, given the relatively low emissions of the Smoking Hills, a volcanic source is suggested as the dominant origin to this factor~~.

The coincident enhancement of MSA production within the ice-free biogenically-active Arctic Ocean in the fall would explain why MSA was also found to be loaded onto this factor. Photochemical SO$_4^{2-}$ apportionment sources have been observed in some previous apportionment studies, though not as commonly as other factors (e.g., Sirois and Barrie, 1999). Significant volcanic influences on Arctic aerosol have also been noted by previous apportionment studies (VanCuren et al., 2012).

Previous analysis of snow and atmospheric samples over this campaign (Macdonald et al, 2017) found SO$_4^{2-}$ to exhibit an enhanced deposition velocity relative to BC, especially during the warm fall months. Typical internally-mixed anthropogenic particulate SO$_4^{2-}$ and BC would be expected to exhibit similar deposition velocities; thus, this discrepancy supported a distinct fall source of SO$_4^{2-}$ which was more readily scavenged/deposited than BC. It is possible that heightened scavenging of volcanic SO$_2$ emissions in the warmer fall resulted in this seasonal trend and the identification of a separate non-anthropogenic SO$_4^{2-}$ factor.

Within a six-factor solution, Factors 6 and 7 were~~Factor 7 showed a distinct maximum in September/October and a low contribution throughout the remainder of the campaign. The contribution calculated for this factor correlated well with measurements of the non-apportioned analytes NO$_2^-$, H$^+$, and Ba. Acids are a large component of volcanic and Smoking Hill emissions and Ba has been associated with coal burning (Berg, Røyset, and Steinnes, 1994; AMAP, 2006). Furthermore, a neutralization ratio of 0.17 was calculated for this factor suggesting an acidic aerosol. The seventh factor also showed a~~

~~correlation with temperature and hours of sunlight. This supported both a biogenic/photochemical source, which would be more active in the warmer months, and a volcanic/Smoking Hills source, which would emit SO_2 and require an oxidizing atmosphere for conversion to SO_4^{2-}.~~

~~The potential source regions of Factor 7 were dominated by local Arctic areas (Figure 2). In particular, ice-free areas of the Arctic Ocean were found to have a significant impact, supporting a marine biogenic contribution. The Bárðarbunga volcano in Iceland and the Smoking Hills in Canada appeared to be the most probable non-marine sources to this factor. Moreover, Bárðarbunga activity was observed by others to diminish in February 2015 (Icelandic Met Office via Global Volcanism Program, retrieved March 2016 from http://volcano.si.edu/). This decline in volcanic activity may explain the negligible contribution of Factor 7 observed in the spring, despite the similar transport and meteorological conditions as the fall.~~

~~Factor 7 appeared to be predominantly a volcanic source, based on SO_4^{2-} loading, potential source regions, and records of simultaneous volcanic activity. Within a six-factor solution, Factors 6 and 7 are~~ essentially combined into a single factor. This combined factor did not exhibit a clear distinct source region, nor was it easily interpretable. The six-factor solution also did not predict the observed distinct fall peak in SO_4^{2-} (as shown in supplemental Figure S7). Thus, the use of a seven-factor solution vastly improved SO_4^{2-} apportionment for this campaign. ~~Photochemical SO_4^{2-} apportionment sources have been observed in some previous apportionment studies, though not as commonly as other factors (Sirois and Barrie, 1999).~~

3.3 Overall Apportionment

~~An overview of each factor and its proposed identity is provided in Table 3. The total residence time by major region is also presented for each factor. All factors were observed to reside primarily in Arctic source areas, due to the predominant transport of air masses over the Arctic Ocean. The sources associated with BC were of particular interest to this study, due to its importance in the Arctic climate. Although each factor is potentially an amalgamation of several co-emitted or co-aligned sources, evidence has been presented that the dominant source of BC, Factor 3, is primarily the product of fossil fuel combustion. When combined with the BC attributed to the industrial source Factor 6, 73% of BC at this site is found to be predominantly the product of fossil fuel combustion (bootstrapping provides a range of 59%-100%). Although biomass burning has previously been argued as the dominant source of BC to more southern Arctic snow (Hegg et al., 2009; Hegg et al., 2010), only 17% of BC was loaded onto the factor most resembling biomass burning, Factor 4~~Considering Figure 3 and Table 2, the apportioned factors can be split into two groups by potential influence/source regions: those dominated by anthropogenic sources and those by natural sources. All factors showed a significant influence from Arctic regions since all trajectories were initialized at Alert, but three factors showed heightened influence from areas outside of the Arctic: Factor 3 black carbon, Factor 5 nitrate, and Factor 6 non-crustal metals. All three were observed to have potential areas of influence extending south into Eurasia, up to and below 45 °N. Although each factor is potentially an amalgamation of several co-emitted or co-aligned sources, per the discussion above, the composition and peak periods of Factor 3, BC, and Factor 6, non-crustal metals, suggest they are primarily anthropogenic in origin. While Factor 5 appears to represent the distinct NO_3^- atmospheric chemistry, the precursors to these reactions may also be anthropogenic in origin. Factor 1, sea salt, also showed a large influence area within the northern Eurasia (per Table 2); however, it is believed that this represents influence from the coast during ice-free periods. Thus, Factor 1 sea salt, Factor 2 crustal metals, Factor 4 carboxylic acids, and Factor 7 sulphate, all appear to be dominated by influences/sources north of 65 °N. Per the discussion above, these factors all appear to have largely natural sources, although additional evidence on the identity of Factor 4 and 7 in particular is warranted. Based on these identifications the rough proportion of each analyte apportioned to factors which most closely resemble anthropogenic sources (Factor 3 BC, Factor 5 nitrate, and Factor 6 non-crustal metals) or natural sources (Factor 1 sea salt, Factor 2 crustal, Factor 4 carboxylic acid, and Factor 7 sulphate) can be estimated. Table 3 provides a summary of this classification.

Table 3 indicates that NO_3^-, BC, Sb, and Pb are likely all dominated by anthropogenic sources. In contrast, Mg^{2+}, Se, Al, Na^+, V, formate, acetate, Cl^-, SO_4^{2-}, NH_4^+, and K^+ are all likely dominated by natural sources. The total apportionment of As, $C_2O_4^{2-}$, MSA, Br-, and Cu to anthropogenic and natural-resembling factors was found to be uncertain based on the bootstrapping analysis. Most notable in this analysis was the apportionment of BC, SO_4^{2-}, V, and Se. While the loading of BC is known to vary between anthropogenic and natural sources by location and season, typically SO_4^{2-}, V, and Se would be expected to be primarily anthropogenic in origin. Figure 4 summarizes the apportionment of BC, SO_4^{2-}, and V over the campaign. The apportionment of Se was similar to that of V.

Table 3: Overview of analyte apportionment.

Factor	1 Sea Salt	2 Crustal Metals	3 BC	4 Carboxylic Acids	5 Nitrate	6 Non-crustal Metals	7 Sulphate	Total Loading by Most-Closely Resembled Source Type: Primarily Anthropogenic (Factors 3,5*,6)	Total Loading by Most-Closely Resembled Source Type: Primarily Natural (Factors 1,2,4*,7*)
Analyte	Loading (mass/mass)								
BC	5%	0%	66%	17%	0%	8%	5%	73% [60-124%]	27% [3-67%]
MSA	5%	0%	10%	12%	27%	4%	42%	41% [6-128%]	59% [26-176%]
ACE	0%	5%	10%	79%	0%	0%	6%	10% [8-75%]	90% [51-155%]
FOR	0%	10%	0%	80%	1%	8%	0%	9% [3-69%]	91% [50-151%]
Cl^-	79%	3%	7%	2%	2%	2%	5%	11% [7-40%]	89% [69-110%]
Br^-	34%	0%	0%	26%	23%	15%	4%	37% [2-108%]	63% [30-138%]
NO_3^-	0%	10%	4%	0%	86%	0%	0%	90% [64-111%]	10% [4-58%]
SO_4^{2-}	10%	4%	5%	0%	4%	9%	68%	18% [14-76%]	82% [62-141%]
$C_2O_4^{2-}$	27%	8%	9%	8%	14%	22%	12%	45% [27-83%]	55% [30-116%]
Na^+	79%	4%	0%	2%	0%	7%	9%	7% [4-41%]	93% [73-118%]
NH_4^+	15%	2%	17%	47%	5%	5%	8%	28% [25-80%]	72% [41-111%]
K^+	38%	10%	0%	4%	20%	10%	19%	29% [8-93%]	71% [36-143%]
Mg^{2+}	43%	34%	1%	5%	0%	0%	17%	1% [1-37%]	99% [76-126%]
Al	2%	84%	0%	0%	3%	3%	7%	7% [2-43%]	93% [70-136%]
V	2%	84%	1%	1%	3%	5%	5%	9% [3-47%]	91% [68-130%]
Cu	6%	48%	0%	0%	7%	28%	11%	35% [19-82%]	65% [32-143%]
As	5%	44%	7%	0%	0%	44%	0%	52% [15-109%]	48% [38-106%]
Se	0%	81%	2%	1%	0%	3%	12%	6% [2-44%]	94% [69-141%]
Sb	0%	0%	4%	18%	1%	60%	17%	64% [42-126%]	36% [11-99%]

Pb	4%	25%	8%	8%	0%	53%	2%	61%	[35-95%]	39%	[27-108%]

Notes: Factors classified based on available evidence as most closely resembling anthropogenic sources (Factor 3, 5, and 6) or most closely resembling natural sources (Factor 1, 2, 4, and 7); however, all factors likely represent an amalgamation of different sources. * Denotes particular uncertainty in classification. Loading described as: optimal solution [25th - 75th bootstrapping].

As discussed above, Arctic BC is often considered to be primarily anthropogenic in origin over the winter season; however, there is some contradictory evidence. It would appear that the sources of BC to Arctic snow vary by location, season, and year. Figure 4 shows that snow BC in this study was dominated by Factor 3, believed to be predominantly anthropogenic in origin. Only about 17% of BC was loaded onto the factor most resembling biomass burning, Factor 4 carboxylic acid, similar to the findings of previous modelling and composition-based apportionment estimates for particulate matter (Slater et al., 2002; Flanner et al., 2007; Skeie et al., 2011; Wang et al., 2011; Yttri et al., 2011; Yttri et al., 2014). The dominant factor for BC varied over the campaign: Factor 3 (BC) was dominant from November through April, but Factors 4 carboxylic acids and Factor 7 sulphate showed larger contributions in the fall and spring. However, given the low levels of BC observed over fall and spring, the absolute contributions of Factor 4 and 7 were small and susceptible to significant uncertainty. The portions of BC assigned to Factors 1 ~~(Marine Elements),~~sea salt and Factor 2 ~~(Crustal Metals), and 7 (Sulphate)~~crustal metals likely represent a regional background level of BC and therefore are likely the combined product of both anthropogenic and natural emissions.

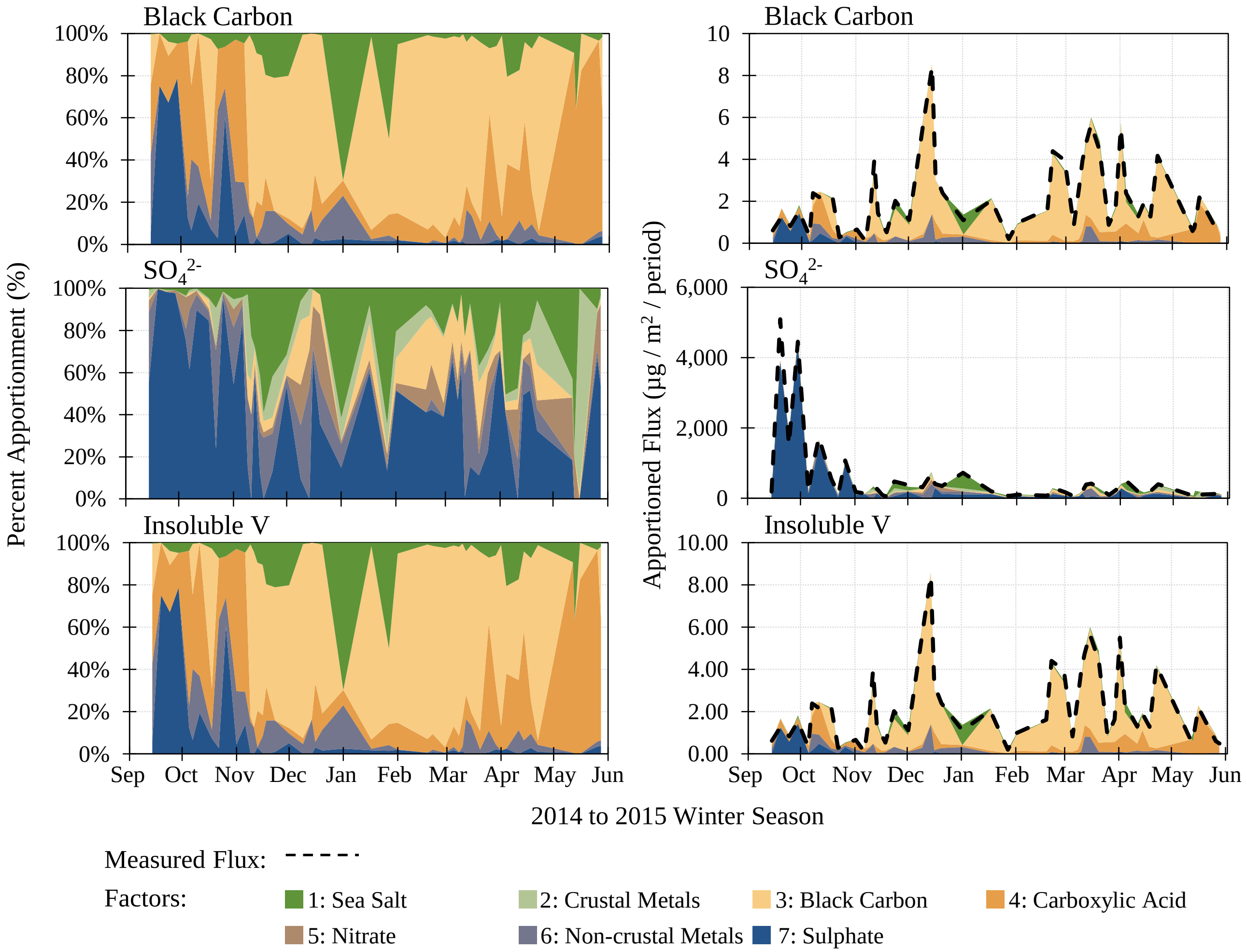


Figure 4: Percent and total apportionment of BC, SO_4^{2-}, and V in snow over the 2014/15 campaign.

The SO_4^{2-} signal was dominated by a fall peak primarily loaded onto Factor 7. While additional evidence is required to corroborate the identity of this factor, the coincidental eruption of Bárðarbunga in Iceland may suggest a significant volcanic source during the fall of this campaign. The absolute flux of SO_4^{2-} in the winter and spring was relatively small compared to the fall peak and mostly comprised of Factor 1 sea salt and Factor 7 sulphate. However, episodic peaks in Factor 3 BC and Factor 6 non-crustal metals suggest influence from anthropogenic plumes. Excluding the September/October peak, the SO_4^{2-} loading is approximately 39 % anthropogenic (12% Factor 3 BC, 9% Factor 5 nitrate, and 18% Factor 6 non-crustal metals) and 61% natural (23% Factor 1 sea salt, 10% Factor 2 crustal metals, 0% Factor 4 carboxylic acid, and 28% Factor 7 sulphate). Thus, factors considered anthropogenic account for about 50% of the non-sea salt SO_4^{2-} signal over this period. If Factor 7 were miss-identified as natural, then approximately 67% of SO_4^{2-} or 87% of non-sea salt SO_4^{2-} over the winter/spring would be considered likely anthropogenic in origin.

Both V and Se are typically considered to be tracers of anthropogenic activity, specifically oil and coal combustion (These factors were

identified based on composition, seasonaggan, 1953; Rahn, 1971; Berg, Røyset, and Steinnes, 1994; Laing et al., 2014). However, the dominant sources of V and Se observed in this study was soil in Factor 2 crustal metals. The loading of these metals relative to Al appeared consistent with the range previously observed by others in soils; also, the raw concentration measurements of these metals showed high correlation with Al. Thus, the apportionment of these metals to primarily natural sources is considered reasonable. As shown in Figure 4, V shows episodic peaks in Factor 5 nitrate, Factor 6 non-crustal metals, and Factor 7 sulphate. Both Factor 5 and 6 are believed to be predominantly anthropogenic in origin; thus these peaks may represent episodic plumes from oil/coal burning activities. However, as shown in Table 3, the total loading of V and Se to these factors are low.

In general, the apportioned analytes differed in how exclusively they were attributed. Some analytes were found to be predominantly loaded onto a single factor: BC, sea salt, and crustal ~~particles~~metals. This may indicate that much of the mass of these analytes exist in externally mixed particles, or internally mixed with a relatively small coating mass. In contrast, other analytes were found to be loaded more evenly onto several factors: MSA, Br^-, K^+, and $C_2O_4^{2-}$. Thus, these analytes may exist primarily as internally mixed particles or gas-phase compounds. This assessment is in agreement with previous explorations in the deposition characteristics of this data (Macdonald et al., 2017).

~~Although BC was apportioned primarily to Factor 3 overall, its main source changed over the collection campaign. Figure 4 shows the apportionment of BC across the 2014-15 season (Factors 2 and 5 are omitted as they were predicted to have zero contribution to BC). Factor 3 (BC) was dominant from November through April, but Factors 4 (Carboxylic Acids) and 7 (Sulphate) showed larger contributions in the fall and spring. However, given the low levels of BC observed over fall and spring, the absolute contributions of Factor 4 and 7 were small and susceptible to significant uncertainty, as shown in Table 3. In general, most analytes were found to exhibit similar source profiles over the campaign. The most notable variability in~~

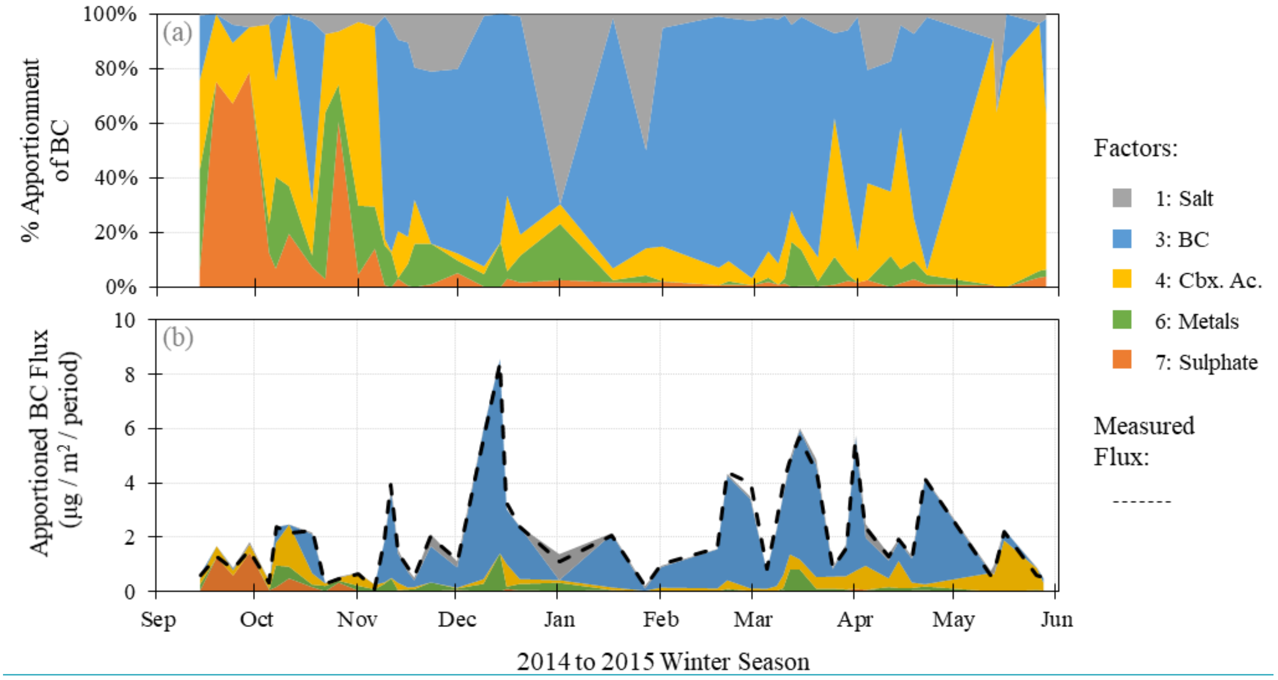
~~Table 3: Overview of factor source regions and BC apportionment.~~

~~Factor~~	~~Dominant Composition~~	~~Source Region % Residence Time~~				~~BC Loading~~	~~Proposed Dominant Identity~~
		~~Arctic~~	~~North America~~	~~Eurasia~~	~~Southern Oceans~~		
~~1~~	~~Na^+, Cl^-~~	~~84%~~	~~1%~~	~~14%~~	~~2%~~	~~5%~~ ~~[0-10%]~~	~~Sea salt~~
~~2~~	~~Al, V, Se~~	~~92%~~	~~1%~~	~~5%~~	~~2%~~	~~0%~~ ~~[0-21%]~~	~~Regional dust~~
~~3~~	~~BC~~	~~85%~~	~~0%~~	~~14%~~	~~1%~~	~~66%~~ ~~[54-74%]~~	~~Mixed Eurasian fossil fuel combustion~~
~~4~~	~~FOR, ACE~~	~~94%~~	~~2%~~	~~1%~~	~~3%~~	~~17%~~ ~~[0-24%]~~	~~Mixed carboxylic acid sources~~
~~5~~	~~NO_3^-~~	~~83%~~	~~0%~~	~~16%~~	~~1%~~	~~0%~~ ~~[0-19%]~~	~~Eurasian anthropogenic emissions and regional complex processing~~
~~6~~	~~Sb, Pb, As~~	~~82%~~	~~0%~~	~~17%~~	~~1%~~	~~8%~~ ~~[5-31%]~~	~~Eurasian industrial activities~~

~~7~~	~~SO_4^{2-}, MSA~~	~~91%~~	~~3%~~	~~6%~~	~~1%~~	~~5%~~ ~~[0-12%]~~	~~Regional volcanic and marine biogenic activity~~

~~Notes: “Southern Oceans” are defined as areas of the Atlantic and Pacific below 65 °N. “Arctic” source area includes the northern Pacific/Atlantic Oceans, Arctic Ocean, Canadian high Arctic, and Greenland. BC loading described as: optimal solution [25th - 75th bootstrapping].~~

~~source profile were observed for BC, as shown above, and K^+, which was dominated by Factor 7 (Sulphate) during the spring/fall and Factor 1 (Marine Elements) during the winter.~~



~~Figure 4: Percent (a) and total (b) apportionment of BC in snow over the 2014/15 campaign.~~

4 Conclusions

The Arctic climate has undergone significant climate change over recent decades and any effort to control and mitigate these changes requires improved understanding of the source contributing to the Arctic snow burden. The data presented here represents an unprecedented campaign of temporally-refined and broadly speciated snow samples which is the first of its kind to be applied to a detail source apportionment analysis. Positive matrix factorization of the snow measurements was found to resolve seven factors with good solution diagnostics, interpretability, and agreement with measured values. These factors were identified based on composition, ~~seasonally~~seasonal contribution, and FLEXPART-predicted major source regions: sea salt, ~~regional dust, mixed Eurasian fossil fuel combustion, North American biomass burning/cloud processing, complex NO_3^- processing, Eurasian industrial activities~~crustal metals, black carbon, carboxylic acids, nitrate, non-crustal metals, and ~~regional volcanic and marine biogenic activity.~~sulphate. Based on possible factor identification, BC apportionment ~~loaded~~was found to load 73% m/m of the total flux onto factors considered to be primarily ~~fossil fuel combustion and Eurasian~~anthropogenic in origin; however, the lower levels of BC in the fall and spring were largely associated with factors which might be associated with North American biomass burning. These ~~findings are in agreement with previous modelled and compositionally estimated apportionments of~~ BC ~~in the Arctic atmosphere, but disagree with high biomass burning loadings of BC observed in previous snow~~ apportionment ~~studies. A predominance of fossil fuel produced BC in~~ results reiterate the ~~Arctic, especially within~~importance in understanding the ~~snow reservoir, could be~~ variation in BC sources by year, location and season. In contrast, SO_4^{2-}, V, and Se were only attributed to factors resembling anthropogenic sources by 18%, 9%, and 6% m/m, respectively. The SO_4^{2-} signal was dominated by a ~~critical driver~~fall peak with limited BC loading. Based on the coincidental eruption of a volcano in Iceland and the lack of anthropogenic tracers, this peak was believed to be predominantly natural in origin. This result may indicate the importance of high volcanic activity years. The low anthropogenic V signal was due to significant loading of V onto a crustal source. The ratios of V and Se to Al in ~~action plans for mitigating regional climate effects.~~ this factor were fairly consistent with the typical range seen in soils; furthermore, the raw measurements of both metals showed high correlation with Al. The anthropogenic signal of V and Se was largely attributed to a factor dominated by non-crustal metals which was believed to represent mixed Eurasian anthropogenic emissions. Comparison of these results to a previous analysis of the deposition characteristics of this data highlighted the importance of relative deposition velocity and mixing state in the apportionment of analytes in snow. Future analyses of Arctic snow would be required to fully understand these complexities.

Author Contribution

Organization of the snow collection campaign was lead by S. Sharma with the assistance of A. Platt and collection by M. Elsasser. Snow analyses were completed by J. McConnell, N. Chellman, D. Toom, L. Huang, and K. Macdonald with the assistance of A. Chivulescu, Y. Lei, and C.-H. Jeong. Ambient atmospheric monitoring was completed by D. Toom and R. Leaitch. FLEXPART simulations were completed by H. Bozem and D. Kunkel with data analysis assisted by K. Macdonald. PMF analysis was completed by K. Macdonald with input on interpretation from all authors. Dr. G. Evans and J. Abbatt provided oversight for the project, including input on the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

Funding of this study was provided as part of the Network on Climate and Aerosols Research (NETCARE), Natural Science and Engineering Research Council of Canada (NSERC), the government of Ontario through the Ontario Graduate Scholarship (OGS), and Environment and Climate Change Canada. This project would not have been possible without the collaboration of many skilled individuals, including Allan K. Bertram and Sarah Hanna at the University of British Columbia and Catherine Philips-Smith at the University of Toronto.

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