Observations of Atmospheric Chemical Deposition to High Arctic Snow – Response to Anonymous Referee #1

Referee comments received and published: 6 December 2016 (quoted below in blue text)

We thank Referee #1 for their well-thought comments and constructive criticism. The following section recapitulates the referee's comments and provides the authors' response to each point presented by the referee.

Response to Referee #1 Discussion

Referee Comment: This manuscript presents results from a 9-month long campaign that collected samples of freshly fallen snow as soon as possible after each deposition event that occurred at Alert from mid-September 2014 through mid-May 2015. These samples were obtained using a technique that the authors assert allowed estimation of combined wet and dry deposition over the interval between each collection, and were analyzed for BC, major ions, and a large number of trace elements. The authors also use measurements of the concentration of aerosol-associated BC, ions and a smaller number of trace elements made as part of the baseline suite by station staff to explore the transfer of impurities from the atmosphere to the snow.
Response: We thank the reviewer for this summary.

Referee Comment: The data set is quite rich and interesting, however I feel that the interpretation and synthesis does not exploit the data set well. A major problem is the decision to define and rely on the "effective deposition velocity" (EDV) for nearly all of the discussion. The authors acknowledge on page 2 that wet deposition is dependent on a wide range of factors, many of which change from day to day, such that previous theories have never found it useful to consider a wet deposition velocity. Then on page 9 they point out additional reasons that such a construct is bound to obscure critical details relating to the processes removing aerosol associated (and gas phase) impurities from the atmosphere to the snow surface, without presenting a strong argument why ignoring these details is reasonable.
Response: We agree with the reviewer that an "effective deposition velocity" lumps together both dry and wet deposition, and that this term is not commonly used in the literature. We made this point clearly in the original paper, as pointed out by the reviewer. The reason we chose this approach was simply that it is not possible to accurately separate dry and wet deposition via snow collection/analysis of the type performed in this study. However, discussion of this parameter does provide insight on bulk deposition mechanisms and magnitudes, and indicate when these exceed that expected due to dry deposition alone. Thus, the effective deposition velocity provides a holistic view of how deposition processes change over the winter seasons. As well, the "effective deposition velocity" is a quantity that can be readily extracted from GCM or CTM models, for comparison to the data. Section 3.2.1 has been expanded to give greater clarity on the interpretation and use of this parameter. We thank the reviewer for this comment.

Referee Comment: To my mind this bad decision is compounded by focusing on monthly values of the estimated EDV as the highest temporal resolution (but only shown in Figure S3). In the actual manuscript one of the key figures (Fig. 2) shows estimated EDV for BC and ions, but only as box and whisker plots summarizing the full campaign (minus Jan and Feb which were discarded due to concerns about data quality, more on that later). Another key figure (Fig. 4) shows monthly EDV, but lumps all of the different impurities together, obscuring significant differences that are evident in Fig. S3 with no explanation. Likewise, Fig. 5 does include separate EDVs for BC and the ions, but presents statistical summaries for a 3 month warm season compared to 4 month cold season (again, omitting Jan and Feb).

Response: We agree with the referee that higher resolution effective deposition velocities should be included to allow inferences of specific events. However, we believe monthly values allow better insight into the general deposition regime of Arctic aerosol without the complexity of event-to-event variation. The supplemental Figure S3 has been moved to the manuscript as per the suggestion of both referees, now Figure 2. Six-day values have been added to this figure along with their associated uncertainties. Monthly values are still included for the discussion of variance in deposition by composition and temporally. Section 3.2.2 of the manuscript has been revised as follows to address this issue (Page/line in the revised text: 10/12-23):

Revised text: *Monthly effective deposition velocities were used to contrast deposition mechanisms by aerosol composition. A monthly resolution provides insight into the general deposition regime of each analyte, highlighting the impact of bulk deposition characteristics rather than event-specific variability. The variability between aerosol of different composition and the influences of seasonal changes within the Arctic system are simpler to identify without the interference of variability between event-specific conditions. A monthly analysis also facilitates future comparison with modelled results which may not replicate individual events. January and February, 2015, were excluded from the monthly analysis because blizzard and high wind conditions were believed to have caused significant losses of snow from the snow tables during these months (based on operator reports), which would lead to underestimation of these snow flux values. The effective deposition velocity is best suited to analysis across periods of equal length and precipitation volume, since both of these parameters are inherently included when the wet deposition efficiency is converted to an equivalent deposition velocity. With the exception of January and February, the total monthly snow precipitation over the campaign was relatively constant, with a relative standard deviation of 20%.*

Referee Comment: The authors should establish a stronger case for the utility of the EVD, and it should be calculated and presented at the 6-8 day resolution of the aerosol sampling. A revised version of Fig S3 (with approximately 4 times as many data points) should be in the main text, informing most or all of the discussion. In the detailed comments below I will work through the manuscript page by page with a mixture of editorial and content comments. The latter will be based on statements in this draft in relation to the figures that are now included, hence may be less relevant if a revised manuscript focuses on the higher resolution that the data set could provide.

Response: Please see our comments above.

Referee Comment: Before turning to detailed comments I need to raise one other general objection to this draft. The authors claim repeatedly that this data set is unique by virtue of the large number of impurities quantified, that their sampling allowed fluxes to be determined, and that sampling captured all (and only) fresh snow events. I would like to point out that the DGASP campaign at Dye 3 in south Greenland took a very similar approach back in 1988-89, though many of the snow samples were not collected in a way that allowed net accumulation (hence flux) to be quantified. This shortcoming of DGASP sampling was addressed in a long series of summer time campaigns at Summit, Greenland (1989 to at least 2003) that included daily sampling to quantify both concentration and the mass of impurity/unit area in the surface layer of snow (see series of papers by Bergin et al. from the mid 90's with "Flux" in their titles as examples), and was maintained for year round campaigns at Summit in 1997-1998 and 2000-2002 (Dibb et al., 2007). With better hindsight, the authors may want to rephrase the statements in this draft made on page 1, lines 20-21; page 2, lines 1-2; page 3, lines 2-3; page 3, lines 20-22; page 6, line 12; page 7, lines 3-6 (particularly this one!); page 16, lines 3-5.

Response: Referee #1 referred to two studies which provided similar insight to Arctic snow deposition and should be discussed: the Dye 3 gas and aerosol sampling program (DGASP), which collected atmospheric and snow samples in Greenland between August 1988 and July 1989 (Davidson et al. 1993; Jaffrezo, 1993); and the snow flux papers published by Bergin et al. in the mid 1990's, which consisted of two month-long campaigns collecting snow, fog, and dry deposition in Greenland in the summers of 1992 and 1993 (Bergin et al., 1994; Bergin et al., 1995).

The DGASP study was an excellent campaign with interesting results. Specifically, surface snow samples were collected at Dye 3 following each snow fall during the 1988-89 season, conditions allowing. Samples were analyzed for major ions, metals, optical carbon, and particle size distribution (Jaffrezo, 1993). As mentioned by Referee #1, the deposition area was not measured for all DGASP samples; thus, snow flux could not be calculated. Another distinction between the DGASP campaign and this study is the collection strategy: surface snow collection as compared to snow table collection as per this study. Collection of snow samples from the ground introduces the inherent difficulty of determining the appropriate collection depth and distinguishing fresh and aged snow. Snow table collection avoids this concern; however, both techniques are subject to uncertainty due to redistribution of snow by winds. Thus, the deposition area and time period associated with surface samples may be less certain than that those associated with snow table samples. Furthermore, the collection of dry deposition from between snowfalls would likely differ between the techniques. As mentioned in the paper, it is uncertain what portion of this dry deposition would have been collected from the snow table; however, we believe that this collection efficiency would be similar between samples. The collection of such dry deposited material in surface snow samples is even harder to quantify, but would be very dependent on small deviations in the collection depth. Thus, we believe the snow table collection technique distinguishes this paper in its ability to quantify the bulk deposition of chemical species as a flux.

The Bergin et al. papers discussed by the referee are also wonderful studies with valuable insight on deposition within the Arctic. These studies quantified daily snow, fog, and dry deposition to collection surfaces at Summit, Greenland during the summers of 1992 and 1993. Samples were analysed for major ions and particle size. The known collection area and time associated with these samples allowed calculation of the material flux and deposition velocity. The Bergin measurements make an excellent complement to the data of this study as they focus on different seasons (summer as compared to fall/winter/spring). Although the measurements of this study are less appropriate for distinguishing the exact split between deposition mechanisms, they do represent a longer collection campaign and broader suite of analytes. As discussed by Bergin et al. (1995), long-term studies are valuable for accessing the annual inventory of deposition within the Arctic.

References to the DGASP and Bergin et al. studies have been added within the introduction, methodology, and results sections (see specific instances of note below). We apologize for not having these in the paper from the outset.

Bergin, M. H., Jaffrezo, J. L., Davidson, C. I., Caldow, R., and Dibb, J.: Fluxes of chemical species to the Greenland ice sheet at Summit by fog and dry deposition, Geochim. Cosmochim. Ac., 58 (15), 3207–3215, doi:10.1016/0016-7037(94)90048-5, 1994.

Bergin, M. H., Jaffrezo, J., Davidson, C. I., Dibb, J. E., Hillamo, R., Maenhaut, M., Kuhns, H. D., and Makela, T.: The Contributions of snow, fog, and dry deposition to the summer flux of anions and cations at Summit, Greenland, J. Geophys. Res., 100 (D8), 16275–16288, doi:10.1029/95JD01267, 1995.

Davidson, C.I., Jaffrezo, J. L., Mosher, B.W., Dibb, J.E., Borys, R.D., Bodhaine, B. A., Rasmussen, R. A., et al.: Chemical constituents in the air and snow at Dye 3, Greenland — I. Seasonal Variations, Atmos. Environ. A-Gen., 27 (17), 2709–2722, doi:10.1016/0960-1686(93)90304-H, 1993.

Jaffrezo, J. L. and Davidson, C. I.: The Dye 3 gas and aerosol sampling program (DGASP): An Overview, Atmos. Environ. A-Gen., 27 (17), 2703–2707, doi:10.1016/0960-1686(93)90303-G, 1993.

Specific lines discussed by the referee are listed below with the revised text by Page/Line(s) #.

1/20-21

Original Line: *These measurements are a unique data set for comparison to models that incorporate deposition to high Arctic snow.*
Revised Line: Line removed from updated text.

2/1-2

Original Line: *Observations of fresh snow samples are particularly uncommon and previous explorations of snow deposition and scavenging mechanisms have been largely reliant on aged snowpack sampling, modelling, and laboratory tests.*
Revised Line: *Seasonal observations of fresh snow samples are particularly uncommon (e.g., Davidson et al., 1993; Toom-Sauntry and Barrie, 2002; Hagler et al., 2007) and previous explorations of snow deposition and scavenging mechanisms have been largely reliant on short-term or aged snowpack sampling (e.g., Bergin et al., 1995), ice cores (e.g., Legrand and De Angelis 1995), modelling, and laboratory tests*. (2/2-5)

3/2-3

Original Line: *To our knowledge, this is the first time that the composition of freshly fallen snow has been analyzed at high temporal frequency throughout an entire cold season in the high Arctic.*
Revised Line: *To our knowledge, this is the first time that the composition and flux of freshly fallen snow has been analyzed at high temporal frequency throughout an entire cold season in the high Arctic*. (3/4-5)

3/20-22

Original Line: *This ability to assign a precise deposition area and time period to each sample, minimizing the inaccuracies introduced by extensive snow redistribution by winds or snow sublimation/melt, was a considerable advantage over previous sampling campaigns of aged snowpack.*
Revised Line: *The collection of fresh snow samples reduces the impact of snow sublimation and/or melt as well as the movement of chemical species between snow and air, which can be a concern for snowpack sampling; however, some bi-directional exchange between snow and atmosphere is unavoidable and natural within natural snowpack systems. Also, the collection of samples from a snow table eliminated the need to estimate the depth of fresh snow, a source of uncertainty for traditional surface snow sampling. This ability to assign a well-defined deposition area and time period to each sample was an advantage over traditional sampling campaigns of aged snowpack . However, both this and traditional snow collection techniques are prone to the uncertainty introduced by the redistribution of snow by winds. Measurements of snowfall accumulation were not available for the collection site. Snow depths measured at the Alert ECCC station indicate that the snow collected on the tables may have underestimated the total snowfall volume by a factor of approximately 1 to 10; however, the meteorological station and collection site were separated by over 6 km with a 50 m difference in elevation, and there was significant disagreement between operator records of weather and that indicated by the meteorological station (see supplemental S4.2 for details). Thus, it was unclear whether this disagreement was the result of snow loss from the snow table or the natural spatial variability in precipitation, and no correction was applied to the collected snow depth.* (3/28-4/8)

6/12

Original Line: *Unlike traditional snowpack collection campaigns, each sample for this study was collected fresh after a known time and over a known area.*
Revised Line: *Each sample for this study was collected fresh after a known time and over a known area.* (6/15)

7/3-6

Original Line: *Comparison of the measured mean values with previous snow observations by others provided a general corroboration of the measurements (see supplemental Table S7 for details); however, given the limitations of previous snow measurements as discussed above, no extensive comparison of seasonal trends could be conducted.*
Revised Line: *A review of existing Arctic snow measurements found the measured median mixing ratios to fall within expected ranges (see supplemental Table S7 for details); however, it should be noted that the referred data represent a variety of collection and analysis techniques. In general, measurements of this campaign showed salt species and non-crustal metals to be at the lower end of the typical range while SO42- and NO3- were at the higher end. A limited number of seasonal snow collection campaigns were available for comparison of the observed seasonal trend in analytes. The winter peak in BC was similar to that observed by Davidson et al. (1993); however, spring values observed in this campaign were higher than previously seen. The observed seasonal trend in major ions was generally consistent with existing literature (Davidson et al. 1993; Toom-Sauntry and Barrie, 2002). Specifically, a winter peak in sea salt, fall/spring peaks in MSA, and a winter peak in NO3- are all typical. However, the fall peak observed in the NSS-SO42- mixing ratio and spring peak in NO3- were unlike seasonal trends observed previously (Davidson et al. 1993; Toom-Sauntry and Barrie, 2002).* (9/1-10)

16/3-5

Original Line: *Given the rarity of temporally-refined and broadly speciated Arctic snow sampling campaigns, measured deposition magnitudes and insights on deposition mechanisms such as these are valuable for future model validation.*
Revised Line: We have left this line as is. Although the referee has provided some additional references, we still find such campaigns to be uncommon. No similar campaign has been completed in the recent decade.

Response to Referee #1 Detailed Comments

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

1/16

Referee Comment: as noted above "effective deposition velocities" not established, and maybe not useful, a strong case needs to be made later that the concept does have utility, or these calculated values should not be highlighted in the abstract
Original Line: *Comparison with simultaneous measurements of atmospheric aerosol mass loadings yields effective deposition velocities that encompass all processes by which the atmospheric species are transferred to the snow.*
Response: As mentioned above, the analysis of effective deposition velocity provides insight into the general deposition regime of the measured analytes which guides the discussion of this paper. Furthermore, this quantity can be directly compared to GCM and CTM output. Because such models cannot often model individual synoptic events, a monthly averaged value is likely of more utility than individual values alone. That said, the individual measurements are now also included in the paper.

2/25

Referee Comment: dependent on snow type
Response: Editorial comment corrected in text (revised manuscript page/line 2/28).

2/27-29

Referee Comment: not sure what the message of sentence starting "The efficiencies..." is supposed to be
Original Line: *The efficiencies of below-cloud scavenging of gases and particles can be similar at an order of magnitude level, though measurements of gaseous scavenging in particular are infrequent and dependent on composition (McMahon and Denison, 1979).*
Response: This line has been removed from the revised manuscript.

2/30

Referee Comment: Last sentence is quite true, and for pretty good reasons. Why are you bucking the trend?
Original Line: *Hence, wet deposition is not typically described via a deposition velocity.*
Response: As discussed above, the methodology of this study did not allow for accurate split of dry and wet deposition. Thus, a bulk parameter has been presented which allows us to explore the general deposition regime of Arctic aerosols by composition and season. This bulk parameter does provide insight into the degree to which the aerosol transport into snow exceeded that expected due to dry deposition alone.

3/11

Referee Comment: Based on the picture in Fig S2 I strongly suspect that the snow table had a major problem with undercatch if there was any wind at all (not just high winds causing blowing snow). It would have been prudent to check this fairly frequently through the campaign by determining the cumulative accumulation of snow on the ground near the table. At a minimum, determination of SWE from either a small pit or a simple core could have been compared to a summation of the SWE for all of the layers collected off the table. Better would have been to check the inventory (mass/unit area) from snow surface to the ground of selected impurities at some interval (at least monthly), by collecting and analyzing the full column of accumulated snow. In the absence of this kind of validation, you probably need to increase the uncertainty estimate for your impurity fluxes.

Response: These are good points that have now been raised as uncertainties in the paper, in section 2.1.

4/16

Referee Comment: What were the QC runs?

Response: Quality control runs were completed by re-analyzing the calibration solution every set number of samples to quantify any instrument drift. An extended supplemental has been prepared with additional details on the methodology. This includes a description of the QC runs for each analysis in supplemental section S2.2.

4/31

Referee Comment: How, exactly, was "mass recovery precision" determined? Sounds like some kind of yield tracer was added, but no details given.

Response: Mass recovery was quantified by massing the total sample at several stages over the sample preparation and analysis. This was done to confirm no sample was lost throughout handling. An extended supplemental has been prepared with additional details on the methodology, including the following text: "*An average sample mass closure of ±1% was observed over the digestion procedure (i.e., sample mass was measured at all stages of analysis to confirm significant sample was not lost during handling).*" (supplemental section S2.1.3).

5/4-6

Referee Comment: When was this "internal standard" added? Before or after digestion? Did it also serve as the yield tracer to track recovery?

Response: The internal standard was added to the digested solution during analysis. An extended supplemental has been prepared with additional details on the methodology, including the following text: "*An internal standard was included in the ICP-MS analysis to quantify and correct for any instrument drift or inter-sample variability. The SCP Science Int. Std. Mix 1 was selected so as to minimize interference with measured analytes while covering the full analyzed spectrum of mass to charge ratios. This internal standard was added to the digested solution as they were sampled for analysis.*" (supplemental section S2.2)

5/11

Referee Comment: in a class 100

Response: Editorial comment corrected in text (5/10).

5/25-26

Referee Comment: Are U. Toronto MA thesis publicly available? If not, are they citable in ACP?

Response: Pertinent details of this thesis have been moved into the supplemental, section S2, and the reference removed.

6/14-24

Referee Comment: There is a sizeable literature about the problems with surrogate surfaces for the collection of both dry and wet deposition. Some of that should be cited here.

Response: We agree that additional references should be provided here and apologise for not doing so. The following have been added (6/18-19):

Davidson, C. I., Lindberg, S. E., Schmidt, J. A., Cartwright, L. G., and Landis, L. R.: Dry deposition of sulfate onto surrogate surfaces, J. Geophys. Res., 90 (D1), 2123–30, doi:10.1029/JD090iD01p02123, 1985.

Hicks, B. B.: Measuring dry deposition: A Re-assessment of the state of the art, Water Air Soil Poll., 30, 75–90, doi:10.1007/BF00305177, 1986.

Ibrahim, M., Barrie, L. A., and Fanaki, F.: An Experimental and theoretical investigation of the dry deposition of particles to snow, pine trees and artificial collectors, Atmos. Env., 17 (4), 781–88, doi:10.1016/0004-6981(83)90427-4. 1983.

6/24-25

Referee Comment: May want to include comparison between cumulative depth, or cumulative SWE probably better, on the table and at the met station. This would allow the reader some insight into how bad table undercatch may have been (or persuade you to make some correction).

Response: While we agree that the depth of snow captured by the snow tables was likely impacted by winds, we do not believe the local meteorological station provides a better estimate of the actual precipitation depth. The Alert ECCC meteorological stations are over 6 km away with a 50 m difference in elevation. Such a difference in location could lead to significant differences in observed snowfall. Furthermore, observations of the collection station operators showed many instances of disagreement with the meteorological station record. For example, there were periods when the operators noted snowfall and yet the meteorological station saw none, or vice-versa. There were also times when the operators noted blowing snow, yet the meteorological station did not indicate this. Thus, we do not believe that the snow depth measured by the station would be an appropriate comparison to that seen at the collection site. Please see revised line of 3/20-22 above.

However, we have performed a supplementary analysis with the assumption that the snow depths measured at the meteorological station are applicable to the snow collection site. These adjusted median effective deposition velocities ranged from 0.08 to 1.7 cm/s, as compared to 0.03 to 1.1 cm/s using snow table depths. The relative velocities and interpretation of the deposition characteristics remained unchanged.

6/27

Referee Comment: Flux per day over 2-18 days makes no sense for a wet deposition event likely lasting just hours. Understood that you cannot separate wet and dry in this data set, but this contributes to discomfort with the calculated EVDs.

Response: The referee is quite right that the deposition measured does not relate to that of a single snowfall but total deposition over a period. As per the discussion above about the utility of the effective deposition velocity, total flux over a period provides insight into the bulk movement of material in the Arctic atmosphere.

8 (Fig 1)

Referee Comment: Why are there gaps of different lengths and at different times in the time series of BC, ions, and crustal metals? According to section 2.1, anytime one bottle was filled there should have been 3 others (presumably for the different analyses). Problems causing gaps need to be noted and enumerated (probably better in 2.1 than here).

Response: There were events when insufficient snow volume fell to fill all sample bottles. In these cases a sub-set of the samples was collected. The samples collected on each date are listed in Table S1. The following text has been added to section 2.1 “*When insufficient snow volume was available for complete collection, a subset of the replicate samples was collected as listed in supplemental Table S1*.” (3/20-21).

9/13-16

Referee Comment: Why are the much more numerous flights from the 4 NOAA AGASP campaigns or the 5-6 NSF TOPSE flights not included here? My impression is that some of these showed significant gradients in the lowest 3 km. (Note that the special issue of Atmos Environ on DGASP also includes AGASP3 papers and provides access to the earlier ones.)

Response: Although some previous studies have shown the lower Arctic atmosphere to be somewhat more consistent, upon further investigation we agree with the referee that this is not always the case. Therefore, we have rephrased this section as follows to discuss this limitation: "*A caveat to this analysis is that the three deposition mechanisms relate to different atmospheric concentrations, a gradient which is not necessarily captured when the ground-level atmospheric concentration (C_A) is used to calculate the effective deposition velocity: dry deposition affects the lower atmosphere, in-cloud scavenging the cloud layer, and below-cloud scavenging the full below-cloud atmospheric column. Previous observations of vertical profiles in the Arctic have shown notable variability with altitude (Hansen and Rosen, 1984; Leaitch et al., 1989; Spackman et al., 2010; Brock et al., 2011; Sharma et al., 2013). So, the calculated effective velocity includes an intrinsic variability dependent on the vertical atmospheric profile of each analyte.*" (9/30-10/4).

Brock C. A., Cozic, J., Bahreini, R., Froyd, K. D., Middlebrook, A. M., McComiskey, A., Brioude, J., et al.: Characteristics, sources, and transport of aerosols measured in spring 2008 during the aerosol, radiation, and cloud processes affecting Arctic Climate (ARCPAC) Project; Atmos. Chem. Phys., 11, 2423–2453, doi:10.5194/acp-11-2423-2011, 2011.

Hansen, A. D. A., and Rosen, H.: Vertical distributions of particulate carbon, sulfur, and bromine in the Arctic haze and comparison with ground-level measurements at Barrow, Alaska, Geophys. Res. Lett., 11 (5), 381–84, doi:10.1029/GL011i005p00381, 1984.

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.

Leaitch, W. R., Hoff, R. M., and MacPherson, J. I.: Airborne and lidar measurements of aerosol and cloud particles in the troposphere over Alert Canada in April 1986, J. Atmos. Chem., 9, 187–211, doi:10.1007/BF00052832, 1989.

Spackman, J. R., Gao, R. S., Neff, W. D., Schwarz, J. P., Watts, L. A., Fahey, D. W., Holloway, J. S., et al.: Aircraft observations of enhancement and depletion of black carbon mass in the springtime Arctic, Atmos. Chem. Phys., 10, 9667–9680, doi:10.5194/acp-10-9667-2010, 2010.

9/16-18

Referee Comment: Somewhat bad form to use unpublished data to support your position, but beyond that, flights in April are not really informative about stability and stratification in the winter. Recall, you are asserting these data are unique because they include the cold season (see later comments related to your Figs 4 and 5).

Response: We agree with the referee that this is a very good point. The reference to unpublished data has been removed. The discussion of vertical variability has been revised as described in the previous point.

9/21-27

Referee Comment: As noted, assuming you can make a better case for utility of EVDs, I do not like the use of monthly averages here and do not think the final sentence is valid justification. There are a lot of papers focused on the POLARCAT airborne campaigns where global and regional CTMs attempted to simulate day by day, plume by plume in some cases, and more should be expected as part of recent and future campaigns. Modelers are striving to improve their simulations, so if experimentalists provide high resolution records they welcome the challenge of simulating them, however poorly the first round of comparisons turn out.

Response: Yes, we agree that some models are capable of high-resolution results; however, monthly values would be of use to a variety of lower-resolution models and seasonal trends can be compared across models simulating different years. Please refer to response above discussing the use of monthly values within the paper's discussion.

9/28

Referee Comment: As noted earlier, summarizing 7 months in box and whisker plot makes little sense to me.

Response: Please see response above.

10/10-13

Referee Comment: To me, the most puzzling aspect of Fig 2 is why Ca is so much higher than Na, Cl and Mg. This is not even mentioned until page 15 (with no plausible explanation). Similarly, suggesting here that BC, NH_4 and SO_4 seem dominated by dry dep causes some tension with later suggestion that they are serving as CCN (or at least being efficiently scavenged) in S/O/My (Fig 5).

Response: Discussion of the high Ca velocity has been moved to this section (13/15-17). As mentioned in the original manuscript, we do not have sufficient information to make a definite claim as to the processes resulting in the elevated Ca deposition relative to Mg. However, the previous study quoted in the text (Banta et al., 2008) showed that distinct Ca-rich and Mg-rich crustal particles may typically exist within the Arctic. Therefore, we suggest that the discrepancy is a result of differing properties associated with these different crustal sources.

We show that the effective deposition velocities of BC, NH_4^+, and SO_4^{2-} over the colder months fall within the typical range of dry deposition velocities for accumulation mode particles. This indicates that dry deposition is a dominant deposition mechanism for these chemical species over cold months. Within the warmer months, the effective deposition velocities of BC, NH_4^+, and SO_4^{2-} are still relatively low but do show some enhancement above the typical dry deposition range. Thus, we suggest that they experience enhanced contribution from wet deposition over this period. Specifically, this enhance wet deposition may be related to their activity as CCN. However, dry deposition is likely still a significant factor for these species over warm months as well. We do not believe these statements are contradictive.

11/5-6

Referee Comment: Not so sure this is true. The Hi-Vol sampling at Alert used to use cellulose filters (Whatman 41s) which do collect acids with decent efficiency. And for a filter exposed for 6-8 days, seasalt and dust can build up to the point where acids may be collected quantitatively.

Response: The Hi-Vol collection was completed using cellulose Whatman 41 filters, as has been the procedure at Alert for decades (Barrie and Hoff, 1985). We agree that although these filters are intended to sample particles they are subject to both positive and negative artefacts. Gases may adsorb onto the filter or acidic gases may react with alkaline sea salt or dust, if they are present, and thus become part of the sample. Gases may also re-volatilize due the high sample flow, or particles may react with acidic Sulphur species on the filter and be released as a gas. However, given the observed chloride deficit in the Hi-Vol aerosol sample, we suspect that the collection of gaseous species by Hi-Vol sampling was likely not a major contribution.

The text has been revised to clarify that Hi-Vol measurements are likely dominated by particle collection, though not necessarily absent of gaseous aerosol collection.

Original Line: *Due to the nature of the Hi-Vol analysis, the measured atmospheric concentrations include only the particle-phase ambient species; however, snow can scavenge both the particle and gas phases, and thus snow samples provide a composite measurement of both.*

Revised Line: *It is expected that the Hi-Vol measurement technique would collect predominantly atmospheric particles, while snow would scavenge both gaseous and particulate aerosol* (12/17-18).

Barrie, L. A., and Hoff, R.M.: Five years of air chemistry observations in the Canadian Arctic, Atmos. Environ., 19 (12), 1995–2010, doi:10.1016/0004-6981(85)90108-8, 1985.

10/7 to 11/8

Referee Comment: Chloride deficit in MBL aerosol and excess in Arctic snow (especially in summer) has been well documented by many others in addition to Toom-Sauntry and Barrie, 2002. This section seems too long for significance of the point being made, but also lacking references to prior work.

Response: We agree that this section need not include such a detailed discussion of chloride deficit. The bulk of this discussion and associated plot have been moved to the supplemental. Furthermore, additional references have been added (12/11):

Barrie, L. A., and Hoff, R.M.: Five years of air chemistry observations in the Canadian Arctic, Atmos. Environ., 19 (12), 1995–2010, doi:10.1016/0004-6981(85)90108-8, 1985.

Quinn, P. K., Bates, T. S., Schulz, K., and Shaw, G. E.: Decadal trends in aerosol chemical composition at Barrow, AK: 1976–2008, Atmos. Chem. Phys., 9, 18727–43, doi:10.5194/acpd-9-18727-2009, 2009.

12/14

Referee Comment: enhanced deposition

Response: Editorial comment corrected in text (13/12).

12/18-21

Referee Comment: As pointed out in first sentence of this paragraph, everything shown in Fig 2 has higher EVD than BC, so what is so special about these 4? They are not as enhanced as Ca in the median, and max EVD for K, Mg, C2O4 and Ca are all higher than the max for MSA, Br and Cl. I agree that the 4 you highlight can have appreciable gas phase, but that is not something discovered or even really supported by Fig 2.

Original Line: *Gas-phase deposition to snow is suggested to contribute to the observed enhanced velocities of methanesulphonate (MSA), Br, Cl, and* NO_3 *relative to BC, either due to gas-phase emissions or gas-phase partitioning during aerosol aging followed by subsequent deposition.*

Response: As stated by the referee these four analytes were specified as they can all have appreciable gas phase. We do not claim to have discovered this point, and believe the text reflects this. Rather we have simply shown that our observations are consistent with this and that the gas-phase deposition can be an important factor in the bulk deposition of chemical species within the Arctic.

Pages 12-14 (Figs 4 and 5)

Referee Comment: As noted at top, I like that 4 at least shows monthly resolution, but don’t like lumping all impurities, while 5 is nice in showing BC and all ions, but is averaging over too much time.

More importantly, I think both are missing key point (which calls the value of EVD into question). Perhaps the most important feature of the Arctic is the huge seasonal contrast in daylight, which leads to big contrasts in energy balance and atmospheric stability. In the winter the atmosphere is extremely stable with weak vertical mixing. Atmospheric impurities that get into the BL tend to be trapped there, and concentrations can be high. As things warm up the BL deepens and concentrations tend to decrease close to the surface. This is clearly reflected in Table S8 which shows very low concentrations of BC, Cl, C_2O_4, Na, K, Mg in SOMy compared to the colder months. Pattern is not so strong for NO_3, NH_4 and SO_4, but the averages for the 3 warm months are quite low compared to the 6 (or 4) cold ones. Part of this may be transport related, and local biogenic emissions may account for the weaker trend in SO4 and opposite trend in MSA, but dilution into a much deeper BL is probably an important factor.

As a thought experiment, given constant monthly accumulation of snow, and constant burden of impurities in the BL, and assuming complete cleansing of the BL over each month, but a 5-10 fold deeper and well mixed BL in warm months compared to cold ones, what would the EVDs look like. Constant monthly flux to snow divided by 5 (or 10) fold lower aerosol concentration measured at surface would yield 5 (or 10) times larger EVD in the warm months. Clearly, the story is not so simple. But, is it really plausible that scavenging in mixed phase clouds is the major factor accounting for increase in BC and all the ions (which should all behave differently in cloud)?

See again the suggestion to include a higher resolution version Fig S3 as the focus of discussion, and exploit the differences to gain insight.

Response: The focus of our discussion is the seasonal variation in bulk deposition processes. We agree that there is significant and interesting variability in deposition at an event resolution; however, the influences on individual events are very complex and cannot be accurately judged without additional information. A holistic view of the scavenging and deposition process can be obtained through analysis and discussion of monthly values to provide insight into their gross mechanisms and better differentiate seasonal trends from the random variability between snowfall events. We have added high-resolution data to the manuscript to guide discussion and future research, but have kept seasonal variation as the focus of our analysis.

We agree that the boundary layer height could be an influence on deposition, as stated by the referee. We have obtained radiosonde measurements from Alert to better characterize the vertical profile. This added analysis is described in section 2.2 in the revised manuscript. Briefly, temperature and relative humidity profiles were used to estimate the mixing height and cloud height over the collection campaign. Both these parameters were considered as potential influences on the deposition process: mixing height essential as a dilution factor on the ambient concentration, and cloud height as a controlling factor on the height of the atmospheric column scavenged by below-cloud wet deposition. These characteristics have been added to the revised Figure 4 and compared to the observed trends in deposition velocity. While the heights do show moderate correlation with the effective deposition velocities, their correlation is lower than that of temperature. Furthermore, the heights are observed to be primarily episodic, unlike the distinct seasonal exhibited by temperature. Hence, the hypothesis that cloud phase may be an important factor in seasonal changes in deposition processes over the cold season was maintained. Furthermore, the radiosonde data showed temperatures above -20 °C to be common within the cloud layer in the warmer months. This supports the potential presence of mixed-phase clouds during this time.

Observations of Atmospheric Chemical Deposition to High Arctic Snow – Response to Anonymous Referee #2

Referee comments received and published: 6 January 2017 (quoted below in blue text)

We thank Referee #2 for their many excellent suggestions and comments. The following section recapitulates the referee's comments and provides the authors' response to each point presented by the referee.

Response to Referee #2 Discussion

Referee Comment: This manuscript describes measurements of the chemical composition of freshly precipitated snow from Alert, Canada and relates those snow measurements to aerosol measurements to derive deposition velocities for various species. The manuscript reads well, and describes a unique contribution to the literature and thus is appropriate, after revision for eventual publication in ACP. The work also uses a comprehensive set of multi-species analyses (BC, IC, ICP-MS) that are a valuable expansion on prior work. However, the presentation could be improved and expanded and the link to past work in this area should be more clearly presented in the main publication.

Response: We thank the referee for their comments.

Referee Comment: Citations to past work are under-done in main text. An example is the work of Toom-Sauntry and Barrie (2002), which described a multi-year weekly snow sampling program from Alert, which is quite similar to this work (with average of 4 day sampling) and should certainly be mentioned in the introduction, but is not. Work at ice core sites (e.g. Summit Greenland, Antarctica) also should be mentioned even if not at the time resolution of this study.

Response: We agree with the referee and have added these references to the papers (Page/line within the revised text: 2/2-5).

Referee Comment: The analysis in this manuscript is presented mostly as a deposition velocity, the ratio of two measured quantities (e.g. Figs. 2, 4, and 5), but the individual parts of this ratio (numerator and denominator) are not discussed as fully. Because both the numerator and denominator go through annual cycles, it is useful to include discussion of both quantities. Specifically, the fall into winter aerosol increase and spring into summer transition is a time of drastic decrease in aerosol loading (e.g. March-May 2015 in Supplemental Table S8), which causes an increase in deposition velocity through equation (1). It would be useful to present graphically in the main text the cycles shown in Table S8 in reference to the snow measurements in Fig. 1. In this way, the scavenging ratio can be better understood. There is also a complementarity between high scavenging and low atmospheric aerosol abundance which can be seen in the data and should be discussed. For example, an very crude order of magnitude of the aerosol lifetime can be estimated by the ratio of the boundary layer height divided by deposition velocity. For sulfate in winter, with v_dep = 0.08, and crudely estimated 1 km boundary layer height, this gives 14 days, and it shortens to 5 days for the "edge seasons" (S/O/My).

Response: We agree that including the individual data, both ambient and snow flux, in the paper is appropriate, along with the derived deposition velocities. The discussion of snow measurements in section 3.1 has been extended. Higher resolution atmospheric measurements have been added to the supplemental, now section S3, and briefly discussed within the text, section 3.1. Although a decrease in atmospheric concentration is related to increased deposition velocity given constant flux, we believe it is important to note that this is a complex process and flux would not necessarily remain constant under reduced atmospheric loads. The deposition velocity is related to the processes controlling deposition, not just the absolute magnitude of the ambient aerosol load.

The thought exercise proposed by the referee is useful as a high level comparison between chemical species. However, the Arctic system is especially complicated by long-range transport and persistent inversion layers which make calculation and interpretation of aerosol lifetimes very difficult. We worry that simplistic pseudo lifetimes as suggested by the referee may be misconstrued by readers and lead to confusion. Therefore, we have not added this discussion to the manuscript.

Referee Comment: Although the method for sampling is unique and useful, it causes "dry deposition" to be a bit different than it might be in true snowpack. This is briefly discussed, but should be more clear. Specifically, as air pumps through actual snowpack, it is filtered by the snow. Harder et al. (1996) indicate that filtering is a significant mechanism of "dry deposition". However, the removal (prior sampling) of old snowpack in the present study causes wind pumping / filtering to not be operative. Thus, the "dry deposition" measured here may be an under-representation of true non-precipitation-related deposition to snowpack. Also, how well particles that dry deposited to the table before snowfall are sampled by scraping off subsequent snowfall is uncertain.

> Harder, S. L., S. G. Warren, R. J. Charlson, and D. S. Covert (1996), Filtering of air through snow as a mechanism for aerosol deposition to the Antarctic ice sheet, J. Geophys. Res., 101(D13), 18729–18743, doi:10.1029/96JD01174.

Response: This is a very good point concerning the dry deposition mechanism via air pumping, and this caveat has been added to the paper.

Revised line: *Furthermore, it should be noted that dry deposition via the filtration of air as it is pumped through the snowpack (as described in Harder et al., 1996) may differ between snow on a snow table and that on the surface.* (4/8-9)

Referee Comment: Another related point is that some fluxes with snow are bi-directional (e.g. snow can re-emit species such as ammonia/ammonium, nitric acid/nitrate, bromide, and mercury. In this study, old snow is removed, so emissions from snow are not measurable (and all deposition fluxes are necessarily positive). This could affect interpretation of ammonium, nitrate, and bromide, and should be mentioned for mercury even through their analysis methods did not quantify it. These processes happen in the actual snowpack, and exclusion of consideration of snowpack emissions would make the deposition fluxes measured here overestimates of the net flux for these species.

Response: This point has been mentioned in the revised version of the paper and we have also revised the text to recognise that re-emission of deposited species from the snow that we do study are still operative, i.e. some bi-directional activity may be occurring during the timescale over which the snow sits on the snow table.

Revised Line: *The collection of fresh snow samples reduces the impact of snow sublimation and/or melt as well as the movement of chemical species between snow and air, which can be a concern for snowpack sampling; however, some bi-directional exchange between snow and atmosphere is unavoidable and natural within natural snowpack systems.* (3/28-30)

Response to Referee #2 Detailed Comments

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

1/17

Referee Comment: The first instance of the word "which" should be replaced by "that" to read "...deposition velocities that encompass all..."
Response: Editorial comment corrected in text (revised manuscript page/line: 1/19).

3/22

Referee Comment: Although loss of snow from the table before sampling is mentioned later, it also needs to be discussed here.
Response: This change has been made (4/1-8).

4/10

Referee Comment: This reference to a thesis (which is not peer reviewed and may not be always accessible) should be replaced by a brief discussion in the supplemental material. There should not be references to theses in general.
Response: Pertinent details of this thesis have been moved into the supplemental, section S2, and the reference removed.

6/9

Referee Comment: The actual quantification of the trajectories should be described here (that is a component of methodology) instead of later.
Response: We have moved this section earlier (6/9-12).

6/17

Referee Comment: It is also not clear if analytes deposited to a bare table would be effectively sampled from the table into the bottles, so "early dry deposition" could have a number of uncertainties.
Original Line: "*Firstly, dry deposition at the beginning of each period would fall directly on the exposed clean table rather than onto previously deposited snow. The difference in surface characteristics created unknown uncertainty in the deposition rate and collection efficiency of the initial portion of dry deposition compared to that which deposited onto a snow-covered table.*"
Response: This line is meant to communicate that it was uncertain what proportion of the dry deposition to the bare table (i.e., the "initial portion") was collected. To clarify this point, the line has been revised to "*Firstly, dry deposition at the beginning of each period would fall directly on the exposed clean table rather than onto previously deposited snow. It is unknown what impact these different surface characteristics could have had on the initial deposition rate and collection efficiency. Thus, there is additional uncertainty in the capture of initial dry deposition to the bare table.*" (6/19-22).

6/19

Referee Comment: Are these four occasions of "resuspended" snow the cause of missing data in mid winter discussed later? Make more clear if these refer to the same events.
Response: Events when blowing snow was observed were excluded from this analysis. Beyond these events, there were additional dates in which some or all samples were missed (typically due to limited snowfall volumes). The following sentence

has been added following the line in question to clarify: "*The dates of these blowing snow events are noted in Table S1 as are missed collections.*" (6/25).

7/2

Referee Comment: By "free" form, do you mean "dissociated ionic" form? It would also be useful to give some discussion of whether soluble or insoluble species dominated for various class of metals.

Response: Yes, the terminology "free form", as used in this line, is in reference to the "dissociated ionic" form. This wording has been changed as suggested to provide better clarity (7/2).

A brief discussion of the soluble and insoluble portions measured for ICP-MS metals has been added in section 3.1: "*The metal measurements can be roughly classified into three categories: predominantly insoluble analytes Al and Fe (>50% insoluble over full campaign); variably soluble/insoluble analytes As, Pb, Cu, Ba, Ti, Mn, K, Cd, and Mg; and predominantly soluble analytes Ca, Cr, Co, and Na (<50% insoluble) (in order from least to greatest soluble fraction), excluding analytes with insufficient soluble or insoluble measurements above MDL.*" (7/3-7).

Table 1

Referee Comment: At some point, method detection limits should be discussed, as well as blanks. For example, the use of nitric acid to clean bottles could lead to a high nitrate blank.

Response: An expanded supplemental has been provided with additional details on the methodology and uncertainty analysis. Supplemental section S2.3 now provides the uncertainty calculation used for measurements along with the calculated error fraction, method detection limit, and signal-to-noise for each analyte in Table S6.

9/16

Referee Comment: This unpublished work is not cited properly. Additionally there should be mention of findings that aerosol (particles and gases) vertical distribution are layered in the Arctic (e.g. Brock et al., Atmos. Chem. Phys., 11, 2423–2453, 2011), and older "Arctic Haze" literature.

Response: The unpublished reference has been removed from the text. The text has been revised as follows to incorporate the additional references: "*A caveat to this analysis is that the three deposition mechanisms relate to different atmospheric concentrations, a gradient which is not necessarily captured when the ground-level atmospheric concentration (C_A) is used to calculate the effective deposition velocity: dry deposition affects the lower atmosphere, in-cloud scavenging the cloud layer, and below-cloud scavenging the full below-cloud atmospheric column. Previous observations of vertical profiles in the Arctic have shown notable variability with altitude (Hansen and Rosen, 1984; Leaitch et al., 1989; Spackman et al., 2010; Brock et al., 2011; Sharma et al., 2013). So, the calculated effective velocity includes an intrinsic variability dependent on the vertical atmospheric profile of each analyte.*" (9/30-10/4).

Brock C. A., Cozic, J., Bahreini, R., Froyd, K. D., Middlebrook, A. M., McComiskey, A., Brioude, J., et al.: Characteristics, sources, and transport of aerosols measured in spring 2008 during the aerosol, radiation, and cloud processes affecting Arctic Climate (ARCPAC) Project; Atmos. Chem. Phys., 11, 2423–2453, doi:10.5194/acp-11-2423-2011, 2011.

Hansen, A. D. A., and Rosen, H.: Vertical distributions of particulate carbon, sulfur, and bromine in the Arctic haze and comparison with ground-level measurements at Barrow, Alaska, Geophys. Res. Lett., 11 (5), 381–84, doi:10.1029/GL011i005p00381, 1984.

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.

Leaitch, W. R., Hoff, R. M., and MacPherson, J. I.: Airborne and lidar measurements of aerosol and cloud particles in the troposphere over Alert Canada in April 1986, J. Atmos. Chem., 9, 187–211, doi:10.1007/BF00052832, 1989.

Spackman, J. R., Gao, R. S., Neff, W. D., Schwarz, J. P., Watts, L. A., Fahey, D. W., Holloway, J. S., et al.: Aircraft observations of enhancement and depletion of black carbon mass in the springtime Arctic, Atmos. Chem. Phys., 10, 9667–9680, doi:10.5194/acp-10-9667-2010, 2010.

Figure 2

Referee Comment: I'm confused about what is shown here. It appears that he minimum (presumably the actual lowest value, while prior table showed 25th percentile), median, maximum (similar question). If that is the case, I'm not sure what the "error bars" are. The error bars also seem to be added at the edges of the "box"? Overall, this looks like a "box and whiskers" plot, but it doesn't seem to have the same information as a standard box and whiskers. Please explain further.

Response: The original Figures 2 and 5 have been updated to avoid misunderstanding (now Figures 3 and 5). The new plots do not include a bar and whisker design. Instead each monthly value is plotted as a point with the median and full range ± uncertainty shown.

Figure 4

Referee Comment: In panel a, the "normalized effective deposition velocity" is shown. I'm not sure what that is. The text description doesn't really help much. Is the idea that aerosol particle components are co-deposited and that aerosol particles are internally mixed? Wouldn't I expect all aerosol particle components to then have the same deposition velocity? Figure S3 shows that different components seem to have different average deposition velocities, which could be an indication of external mixture of aerosol components, as was discussed for BC. Some further discussion, and potentially elevation of Figure S3 (or some subset of the species) to the main text would be preferable to the "lumping" that was done in Figure 4, panel a.

Response: The use of normalized effective deposition velocities was simply to allow easier comparison among the analyzed chemical species and to explore a "typical" seasonal pattern. For each analyte the effective deposition velocity for each month was divided by the average effective deposition velocity of that analyte to obtain a normalized value. However, since the supplemental Figure S3 has been moved to the manuscript (now Figure 2), as per the suggestion of both referees, the normalized trend is no longer required for comparison and has been removed. The provided meteorological trends have now been compared to the trends of individual analytes within the revised section 3.2.3.

Figure 5

Referee Comment: I still don't understand the error bars. Please explain.

Response: Please see response to comment on the original Figure 2.

Observations of Atmospheric Chemical Deposition to High Arctic Snow

Katrina M. Macdonald[1], Sangeeta Sharma[2], Desiree Toom[2], Alina Chivulescu[2], Sarah Hanna[3], Allan K. Bertram[3], Andrew Platt[2], Mike Elsasser[2], Lin Huang[2], David Tarasick[4], Nathan Chellman[5], Joseph R. McConnell[5], Heiko Bozem[6], Daniel Kunkel[6], Ying Duan Lei[1], Greg J. Evans[1], Jonathan P. D. Abbatt[7]

[1] Department of Chemical Engineering and Applied Chemistry, University of Toronto, M5S 3E5, Canada
[2] Climate Research Divisions, Environment and Climate Change Canada, Toronto, M3H 5T4, Canada
[3] Department of Chemistry, University of British Columbia, Vancouver, V6T 1Z1, Canada
[4] Air Quality Research Divisions, Environment and Climate Change Canada, Toronto, M3H 5T4, Canada
[5] Desert Research Institute, Reno, 89512, Unites States of America
[6] Institute for Atmospheric Physics, Johannes Gutenberg University Mainz, ~~Becher Weg, 21~~ 55128, Germany
[7] Department of Chemistry, University of Toronto, M5S 3H6, Canada

Correspondence to: Jonathan Abbatt (jabbatt@chem.utoronto.ca)

Abstract. Rapidly rising temperatures and loss of snow and ice cover have demonstrated the unique vulnerability of the high Arctic to climate change. There are major uncertainties in modelling the chemical depositional and scavenging processes of Arctic snow. To that end, fresh snow samples collected on average every four days at Alert, Nunavut, from September 2014 to June 2015 were analyzed for black carbon, major ions, and metals, and their concentrations and fluxes reported. Comparison with simultaneous measurements of atmospheric aerosol mass loadings yields effective deposition velocities ~~which~~that encompass all processes by which the atmospheric species are transferred to the snow. It is inferred from these values that dry deposition is the dominant removal mechanism for several compounds over the winter while wet deposition increased in importance in the fall and spring, ~~probably~~possibly due to enhanced scavenging by mixed-phase clouds. Black carbon aerosol was the least efficiently deposited species to the snow~~. These measurements are a unique data set for comparison to models that incorporate deposition to high Arctic snow.~~

Comment [KM etal1]: Edit as per Referee #2 comment

Comment [KM etal2]: Removed as per Referee #1 comment

1 Introduction and Background

In recent decades drastic changes have been observed within the Arctic, including a rapid increase in surface temperatures and loss of sea ice and snow cover (Rigor et al., 2000; Stroeve et al., 2005; Hartmann et al., 2013). Not only have these changes had adverse consequences for local populations and ecosystems, it has been suggested that their ~~global~~ impacts may be significant at the global scale (Law and Stohl, 2007; AMAP, 2011).~~ Specifically, light~~ Light-absorbing compounds, the most widely-studied of which being black carbon (BC) particles, can have a particularly significant impact on the Arctic atmosphere and snow systems through the absorption of solar radiation and subsequent warming and snow melt (Bond et al., 2013). While the Arctic atmosphere has been previously explored spatially, temporally, and compositionally (e.g., Hartmann et al., 2013), Arctic snow and the mechanisms linking snow to the atmosphere have been the subject of only a relatively small number of studies (AMAP, 2011), despite the enormous amount of research conducted on the Arctic Haze phenomenon (Quinn et al., 2007). ~~Observations~~Seasonal observations of fresh snow samples are particularly uncommon (e.g., Davidson et al., 1993; Toom-Sauntry and Barrie, 2002; Hagler et al., 2007) and previous explorations of snow deposition and scavenging mechanisms have been largely reliant on short-term or aged snowpack sampling~~,~~ (e.g., Bergin et al., 1995), ice cores (e.g., Legrand and De Angelis 1995), modelling, and laboratory tests.

Comment [KM etal3]: Edited in response to Referee #1 comment

Aerosols entering the Arctic atmosphere, either generated locally or transported from elsewhere, can be removed by atmospheric transport or deposition. Deposition of particles follows two mechanisms: dry deposition, whereby particles are deposited to the ground by impaction, gravitational settling, and Brownian motion; and wet deposition, whereby particles are scavenged by hydrometeors and deposited through precipitation. Wet deposition is further split into two scavenging mechanisms: in-cloud scavenging which removes particles from the cloud layer during precipitation formation, and below-cloud scavenging which removes particles from the atmospheric column through which precipitation falls. Gaseous compounds also undergo similar scavenging processes (Seinfeld and Pandis, 2006).

The rate of dry deposition is dependent on the properties of the depositing particle, the surface onto which deposition occurs, and the air-surface boundary layer (Sehmel, 1980; Zhang and Vet, 2006). Dry deposition velocities of accumulation mode particles, the dominant mass-weighted mode of particles observed in the non-summer Arctic (Sharma et al., 2013), to snow have been modelled and observed over a range of 0.01 to 0.60 cm/s, typically within 0.02 to 0.10 cm/s; gaseous deposition velocities to a snow surface show~~s~~ a similar range, with observations from 0.05 to 0.50 cm/s and a typical velocity of approximately 0.10 cm/s (McMahon and Denison, 1979; Sehmel, 1980; Davidson et al., 1987; Hillamo et al., 1993; Bergin et al., 1995; Petroff and Zhang, 2010; Liu et al., 2011). Wet deposition is dependent on the properties of the depositing aerosol and the atmospheric conditions. In-cloud scavenging is largely controlled by a particle's size and composition which dictate its ability to nucleate hydrometeors and to be scavenged by cloud droplets. Particles can act as cloud condensation nuclei (CCN) that nucleate water droplets or ice nuclei (IN) that nucleate ice crystals. Common CCN components include sea salt, sulphate (SO_4^{2-}), and nitrate (NO_3^-), while mineral dust and bioaerosols are common IN (Hoose and Möhler, 2012; Farmer, Cappa, and Kreidenweis, 2015). Typically, BC is considered to be an ineffective CCN or IN (Hoose and Möhler, 2012; Farmer, Cappa, and Kreidenweis, 2015). Although liquid water clouds are not expected during the Arctic winter, mixed-phase clouds, which contain both liquid water and ice, have been observed in this region at temperatures well below 0 °C, in unusual cases down to -40 °C but more commonly between -20 °C and -10 °C (Morrison et al., 2005; Shupe et al., 2006). Below-cloud deposition is dependent on snow type and meteorological conditions, which dictate the volume of air scavenged per snowfall (Zhang and Vet, 2006). Particle size also affects below-cloud scavenging with higher scavenging efficiencies for particles above 2.5 μm diameter relative to accumulation mode particles (Zhang and Vet, 2006). ~~The efficiencies of below cloud scavenging of gases and particles can be similar at an order of magnitude level, though measurements of gaseous scavenging in particular are infrequent and dependent on composition (McMahon and Denison,~~

Comment [KM etal4]: Added as per Referee #1 comment

~~1979).~~ The total wet deposition is a function of the volume of precipitation. Hence, wet deposition is not typically described via a deposition velocity.

Comment [KM etal5]: Removed as per Referee #2 comment

The goals of this paper are to present a new dataset in which the chemical composition of freshly fallen snow was measured through a fall-winter-spring period at a high Arctic field station. By combining these data with simultaneous measurements of ambient aerosol, the efficiency of deposition of individual species from the atmosphere to the snow can be evaluated under a set of broad assumptions. While this paper presents the measurement data set in detail and focuses on the depositional and scavenging mechanisms that can be inferred from it, a subsequent publication will identify potential pollutant sources based on the snow compositional data. To our knowledge, this is the first time that the composition and flux of freshly fallen snow has been analyzed at high temporal frequency throughout an entire cold season in the high Arctic.

Comment [KM etal6]: Edited as per Referee #1 comment

2 Methodology

2.1 Snow Sample Collection

Snow samples were collected at Environment and Climate Change Canada’s (ECCC) Dr. Neil Trivett Global Atmosphere Watch Observatory at Alert, Nunavut from September 14th, 2014 to June 1st, 2015 as part of the Network on Climate and Aerosols Research (NETCARE) initiative to create a temporally-refined and broadly speciated dataset of high Arctic snow measurements. Alert is a remote outpost in the Canadian high Arctic, at the northern coast of Ellesmere Island (82°27’ N, 62°30’ W), with a small transient population of research and military personnel (location details provided in supplemental Sect. ~~S3~~S4). Snow samples were collected from two Teflon-surfaced snow tables (about 1 m^2 by 1 m above ground level, shown in supplemental Figure S2) located in an open-air minimal traffic site, about 6 km SSW of the Alert base camp, 201 m above sea level. Freshly fallen snow was collected from the tables using a Teflon scraper and scoop by dividing the table into rectangular portions for replicate sample collection. Four replicate samples were collected for this study and the table area cleared to fill each bottle was recorded. Prior to their first use and between snow sample collections, both snow tables were fully cleared of all remaining snow and cleaned with methanol. Samples were collected as soon after the end of each snowfall as feasible, conditions allowing. From September 14th, 2014 to June 1st, 2015, 59 sets of snow samples were collected. When insufficient snow volume was available for complete collection, a subset of the replicate samples was collected as listed in supplemental Table S1. The interval between collections varied based on snowfall frequency, ranging from 1 to 19 days with an average of 4 days. The table area and collection period length associated with each sample allowed the measured concentration of each analyte to be converted to a flux. ~~This ability to assign a precise deposition area and time period to each sample, minimizing the inaccuracies introduced by extensive snow redistribution by winds or snow sublimation/melt, was a considerable advantage over previous sampling campaigns of aged snowpack.~~

Comment [KM etal7]: Edited for consistency with revised supplemental

Comment [KM etal8]: Added as per Referee #1 comment

Comment [KM etal9]: Text removed since discussed in new paragraph to follow

New sample bottles were used for the collection campaign and each bottle was thoroughly cleaned prior to use. Bottles and lids were soaked in 5% nitric acid, 1% detergent in water (Alconox), and deionized 18.2 MΩ water (DIW), allowing 10 to 14 hours for each soak. Each dried bottle was then sealed in a protective plastic sleeve until use. At Alert, plastic outer gloves and lab coats were used to minimize contamination during collection, and the scraper and scoop were cleaned with DIW prior to each collection.

The collection of fresh snow samples reduces the impact of snow sublimation and/or melt as well as the movement of chemical species between snow and air, which can be a concern for snowpack sampling; however, some bi-directional exchange between snow and atmosphere is unavoidable and natural within natural snowpack systems. Also, the collection of samples from a snow table eliminated the need to estimate the depth of fresh snow, a source of uncertainty for traditional surface snow sampling. This ability to assign a well-defined deposition area and time period to each sample was an advantage over traditional sampling campaigns of aged snowpack. However, both this and traditional snow collection techniques are prone to the uncertainty introduced by the redistribution of snow by winds. Measurements of snowfall accumulation were not available for the collection site. Snow depths measured at the Alert ECCC station indicate that the snow collected on the tables may have underestimated the total snowfall volume by a factor of approximately 1 to 10; however, the meteorological station and collection site were separated by over 6 km with a 50 m difference in elevation, and there was significant disagreement between operator records of weather and that indicated by the meteorological station (see supplemental S4.2 for details). Thus, it was unclear whether this disagreement was the result of snow loss from the snow table or the natural spatial variability in precipitation, and no correction was applied to the collected snow depth. Furthermore, it should be noted that dry deposition via the filtration of air as it is pumped through the snowpack (as described in Harder et al., 1996) may differ between snow on a snow table and that on the surface.

Comment [KM etal10]: Added expanded discussion to address Referee #1 and #2 comments

Comment [KM etal11]: Edited line as per Referee#1 comment

Comment [KM etal12]: Added as per Referee #2 comment

2.2 Campaign Meteorological Conditions

Comment [KM etal13]: Section added to address Referee #1 comment

Alert station operators ~~also~~ recorded the collection conditions for each sample. Atypical snowfall events were noted: diamond dust events, small crystalline snowfalls; and blowing snow events, periods when high winds potentially resuspended snow from the ground. Operators also made note of any unusual weather conditions such as fog or blizzard conditions. Local ground-level meteorological conditions were monitored by the Alert ECCC stations, approximately 6 km NNE of the collection site (~~Climate~~ station IDs 2400306, 2400305, and 2400302~~) (~~; retrieved Nov. 2015 from climate.weather.gc.ca). In addition to ground-level meteorological information, vertical profiles were monitored via 6 to 12-hour radiosondes. The radiosonde data were used to estimate mixing height and cloud height over the campaign. Mixing height was taken as the lowest altitude corresponding to an inflection point in the potential temperature. If the potential temperature gradient did not change from negative to positive within the lowest 3 km, no mixing height was found. The vertical humidity profiles were used to identify cloud height as the lowest altitude, within 3 km of the surface, with 100% relative humidity. When 100% humidity was not reached, this criterion was relaxed to 95%. Details of meteorology data are provided in the supplemental section S4.2.

2.~~2~~3 Snow Sample Preparation and Analysis

Comment [KM etal14]: Expanded methodology provided in supplemental and reduced detail in manuscript

All snow samples were kept frozen prior to analysis, throughout storage and shipping. A broad suite of analytes was quantified using replicate snow samples from each snowfall: BC, major ions, and metals.~~ The procedures for BC and major ion analysis followed well developed protocols and are described only briefly herein, but the methodology developed for metals quantification is described in greater detail. All snow samples were kept frozen prior to analysis, throughout storage and shipping~~ Detailed procedures are provided in the supplemental S2.

Refractory BC quantification was completed via single-particle soot photometry (SP2) ~~at the Desert Research Institute, Reno, Nevada, ~~as per McConnell et al. (2007). Briefly, ~~snow samples collected in 50 mL Pyrex bottles were ~~melted ~~at room temperature the morning of analysis ~~and sonicated ~~for 1 minute. Each sample was~~snow samples were atomized via Apex-Q nebulizer and dried particles with 0.02 to 50 fg BC were quantified via SP2. Observed BC mass distributions did not suggest significant underestimation of the total BC mass due to this size cut-off~~, (Macdonald, 2016).~~. A quality control standard and analysis blank were analyzed for every batch of 17 samples.

Major ions were measured via ion chromatography (IC) at ECCC, ~~Toronto office, ~~as per Toom-Sauntry and Barrie (2002). Briefly, melted samples ~~collected in 250 mL high-density polyethylene (HDPE) bottles were melted in a warm water bath. Shortly after melting, ions ~~were quantified using a Dionex IC~~ (~~: DX600 for anions and cations, ICS2000 for organic acids~~) with a 200 µL sample loop~~. Aliquots of these samples were also used for pH analysis (Denver pH analyzer). Equipment was calibrated daily and quality control runs completed every ten samples.

Metals analysis was completed via inductively coupled plasma mass spectrometry (ICP-MS) at the University of Toronto. ~~Samples collected in 500 mL HDPE bottles were melted rapidly in a microwave oven and immediately filtered with a 13 mm diameter 0.45 µm cellulose acetate filter (Whatman) using a reusable polytetrafluoroethylene filter holder (Sartorius) and a polyethylene syringe (BD). The full collected volume was filtered for each sample, ranging from 40 to 200 mL meltwater. Both filtrate and filter were analyzed and considered as soluble and insoluble metals, respectively. Samples were digested using 70% nitric acid (HNO_3), ultra trace grade (SCP Science PlasmaPure). Filtrate samples were digested by bringing the solution to 2% HNO_3 mass/mass; however, filter samples required an augmented digestion procedure to enable quantification. It has been shown that microwave digestion significantly improves the recovery of insoluble metals without the need for more hazardous digestion reagents (Swami et al., 2001; Pekney and Davidson, 2005; US EPA, 2007). Each cellulose filter was placed in a polytetrafluoroethylene microwave digestion tube (CEM MARSXpress) with ultra-trace grade 70% HNO_3. Filtrate and filter were sealed and left overnight at room temperature to digest. After a 10 to 15 hr digestion time, DIW was added to each filter vessel to dilute the solution to 2% HNO_3. The filter samples were then placed in a microwave digester (CEM MARS 6) and digested using the US Environmental Protection Agency (US EPA) 3051 procedure for trace metal analysis. The digested filter solutions were transferred to polypropylene tubes and centrifuged to separate any undigested residue. An average mass recovery precision of ±1.5% was observed over the digestion procedure.~~

~~Filter and filtrate samples were analyzed by ICP-MS (Thermo Scientific iCAP Q) under kinetic energy discrimination mode. Dwell times were set to 0.02 s for analytes with an ionization potential less than 9 eV and 0.10 s for analytes with a greater ionization potential. The wash time was set to 75 s and uptake time to 50 s (as per Henry and Wills, 2012; Wang and Miao, 2016).~~Briefly, melted samples were filtered to separate insoluble and soluble metals (considered as that which was retained or passed through a 0.45 µm cellulose acetate filter, respectively). Both filtrate and filter were digested using 70% nitric acid, ultra-trace grade (SCP Science PlasmaPure), and filter digestion was augmented using a microwave digester (CEM MARS 6). Centrifuged samples were then quantified via ICP-MS (Thermo Scientific iCAP Q). A performance test and calibration (SCP Science PlasmaCAL QC Std 4) were completed prior to each run, and quality control checks were completed every ten samples~~ to quantify instrument drift. All concentrated standards were followed by an extra DIW blank to prevent extensive carry-over from standard to samples. An internal standard, selected so as to minimize interference with measured analytes while covering the full analyzed spectrum of mass to charge ratios,~~. Also, an internal standard was included to quantify and correct for any instrument drift or inter-sample variability (SCP Science Int. Std. Mix 1). ~~The full 4.6 to 245 mass/charge ratio (*m/z*) range was scanned and, where necessary, interference corrections were applied (as per Henry and Wills, 2012; Wang and Miao, 2016). It should be noted that this preparation and analysis procedure is not expected to retain highly volatile metals, such as Hg. All apparatus components were thoroughly cleaned before and between uses with HNO_3 and DIW. The microwave digestion vessels underwent a full digestion cycle with 15 mL 70% HNO_3 and then were rinsed with ultra-trace grade HNO_3 and DIW prior to each use. ~~All sample preparation was completed in a class 100 vertical laminar flow cabinet (AirClean Systems AC 632).

Quality assurance is of the upmost importance in the analysis of dilute Arctic samples. Instrument accuracy was confirmed through the analysis of certified reference materials. The uncertainty of each measurement was estimated based on analysis detection limits and reproducibility~~.~~; details are provided in supplemental Sect. S2 (as per Reff et al., 2007; Norris et al., 2014). Also, the signal-to-noise (S/N) of each analyte was calculated to indicate the strength of each measurement~~ (as per Norris et al., 2014). A~~, with a S/N value over ~~2 was~~one considered to be strong (~~Paatero and Hopke, 2003).~~Norris et al., 2014). Regular analysis of blanks was used for background subtraction and to define method detection limits (MDL) as three standard deviations of the blank levels. Beyond typical preparation blanks, which used DIW in the place of snow melt water, field blanks were also analyzed. Once per month, a set of empty sample bottles was taken to the snow table, opened, and resealed without collection. These field blank bottles were stored and shipped with the regular samples and rinsed with DIW to quantify any contamination throughout the sampling process. Any influence from the local Alert base camp was identified using local wind records and the activity logs of the base camp personnel. The only analytes that showed a potential influence from base camp winds were crustal metals, with Pearson's correlation coefficients (R) of 0.4 to 0.6 (p-value 0.0001 to 0.002) between snow mixing ratios and periods of base camp winds. Base camp combustion activity logs showed no significant impact on the samples.~~ Additional methodology details are provided in Macdonald (2016).~~

Comment [KM etal15]: Added as per Referee #2 comment

Comment [KM etal16]: Removed reference to thesis as per Referee #1 and #2 comments

2.~~3~~4 Atmospheric Monitoring

Ground-level atmospheric monitoring data from the Alert Global Atmospheric Watch Observatory were provided by ECCC~~.~~ (see supplemental S3 for details). Atmospheric BC was monitored hourly by SP2 (Droplet Measurement Technology) (as per Schroder et al., 2015) and major ions by IC of 6 to 8-day high-volume filters of total suspended particles (Hi-Vol) (as per Sirois and Barrie, 1999). Both the SP2 and Hi-Vol were operational throughout the campaign with coverages of 92% and 94%, respectively. As ~~for~~in the snow SP2 analysis, the influence of BC particle size cut-off limits was considered but found to have minimal impact, especially when considered at a monthly scale.

2.~~4~~5 Transport Modelling

The Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005) was used to determine the source region of air masses that were measured over Alert. This model has previously been shown to be an effective tool for the prediction of transport pathways into and within the Arctic (e.g., Paris et al., 2009). The simulations were driven using meteorological analysis data from the European Centre for Medium-Range Weather Forecasts with a horizontal grid spacing of 0.25° in longitude and latitude and 137 levels in the vertical. For each 5 day period during the measurement period we released virtual tracers over Alert in four different altitude levels, 100 m, 500 m, 1000 m, and 2000 m above sea level, to distinguish between the levels which may be scavenged by snow. The tracers were then ~~traced~~followed for ten days backward to obtain the source region for the particular time period. The FLEXPART results were used to explore the dominant source regions associated with each sample. As a simple quantification of the variability in source region, FLEXPART trajectories were summarized by the observed southern limit of transport. This southern limit was calculated as the latitude which encircles 98% of the 10-day transport source area. Values were calculated using each of the four initialization altitudes.

Comment [KM etal17]: Moved description up from results as per Referee #2 comment

3 Results and Discussion

3.1 Total Deposition of Arctic Snowfall Events

~~Unlike traditional snowpack collection campaigns, each~~Each sample for this study was collected fresh after a known time and over a known area. Given that the snow tables were exposed to the ambient atmosphere for the entirety of each collection period, the measured deposition is considered to represent the total deposition (wet and dry) for said period~~.~~; however, it is known that surrogate surfaces do not provide an exact proxy for the deposition which would be seen to a natural snow surface (Ibrahim, Barrie, and Fanaki, 1983; Davidson et al., 1985; Hicks, 1986). There are two additional caveats to this assumption. Firstly, dry deposition at the beginning of each period would fall directly on the exposed clean table rather than onto previously deposited snow. ~~The difference in~~It is unknown what impact these different surface characteristics ~~created unknown uncertainty in~~could have had on the initial deposition rate and collection efficiency. Thus, there is additional uncertainty in the capture of ~~the~~ initial~~ portion of~~ dry deposition ~~compared~~ to ~~that which deposited onto a~~

Comment [KM etal18]: Edited as per Referee #1 comment

Comment [KM etal19]: Added as per Referee #1 comment

~~snow covered~~the bare table. Secondly, strong winds can disturb and redistribute the snowpack and cause snow to be blown off and/or onto the snow table. Alert operators recorded four occasions when the snowpack was observed to be resuspended due to high winds and these were excluded from the presented results. ~~Several additional collection periods saw larger snow depths measured by local meteorological stations than that observed on the collection table, implying snow loss from the table. However, as the meteorological station was over 1 km away from the collection site and about 50 m lower in elevation, it was unclear whether this disagreement was the result of snow loss from the snow table or the natural spatial variability in precipitation. Thus, no correction was applied to the collected data based on the meteorological station's snow depth.~~ The dates of these blowing snow events are noted in Table S1 as are missed collections.

Comment [KM etal20]: Revised as per Referee #2 comment

Comment [KM etal21]: Removed since included in revised methodology

Comment [KM etal22]: Added as per Referee #2 comment

The observed snow mixing ratios and fluxes are summarized in Table 1 and Figure 1 for measured analytes with a strong S/N. Mixing ratio is reported as parts per billion by mass (ppb) with the exception of pH. Flux is reported on a per day basis to take into account the differing collection period lengths; however, it should be noted that this length corresponds to the entire collection period (i.e., the number of days between clearing the snow table), not just the length of time when snow was actually falling. A full record of the measured deposition over the campaign is provided in the supplemental (Table S1-6) along with the associated uncertainties and ~~values specific to~~notes of atypical collection conditions. It should be noted that although IC measurements are provided as the measured ions throughout the discussion, these analytes may not necessarily exist in the ~~free~~ dissociated ionic form in the environment. Also, the metal measurements provided in Table 1 are total values, insoluble and soluble. The soluble fractions differed by analyte and by date and are provided in the supplemental (Table S4-6). ~~Comparison of the measured mean values with previous snow observations by others provided a general corroboration of the measurements (see supplemental Table S7 for details); however, given the limitations of previous snow measurements as discussed above, no extensive comparison of seasonal trends could be conducted.~~ The metal measurements can be roughly classified into three categories: predominantly insoluble analytes Al and Fe (>50% insoluble over full campaign); variably soluble/insoluble analytes As, Pb, Cu, Ba, Ti, Mn, K, Cd, and Mg; and predominantly soluble analytes Ca, Cr, Co, and Na (<50% insoluble) (in order from least to greatest soluble fraction), excluding analytes with insufficient soluble or insoluble measurements above MDL.

Comment [KM etal23]: Edited as per Referee #2 comment

Comment [KM etal24]: Removed as per Referee #1 comment

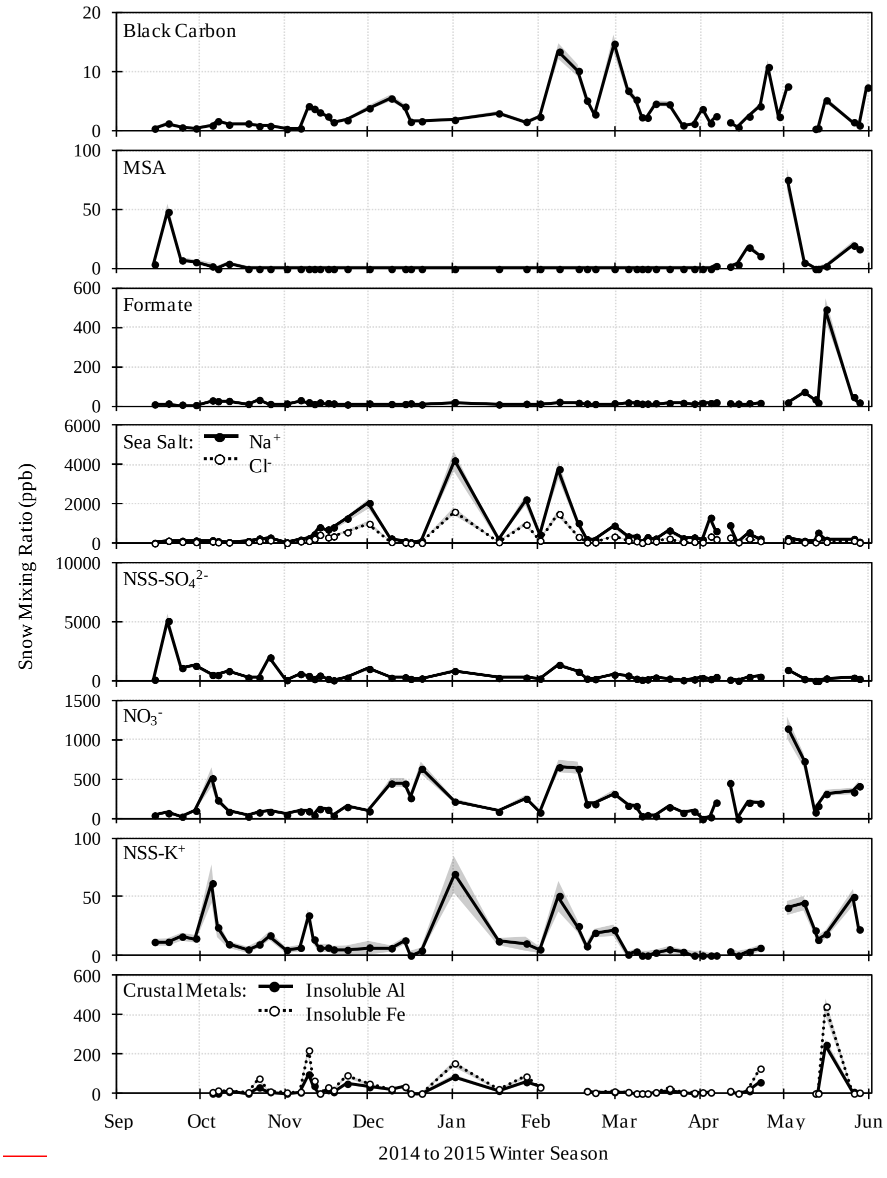
Comment [KM etal25]: Added as per Referee #2 comment

Table 1: Overview of fresh snow composition and inferred fluxes over the 2014-15 winter season.

Analysis	Analyte	Snow Mixing Ratio (ppb)			Snow Flux (µg/m^2/d)		
		25th Percentile	50th Percentile	75th Percentile	25th Percentile	50th Percentile	75th Percentile
SP2	BC	1.3	2.3	4.1	0.24	0.42	0.86
IC	MSA	<1.9	<1.9	2.5	<0.1	<0.1	<0.1
	ACE	9.6	19.9	27.3	1.9	3.5	7.5
	PRP	<1.5	2.2	5.3	<0.10	0.62	2.06
	FOR	8.4	11.0	14.8	1.32	2.66	4.72
	Cl^-	132	249	605	35.6	59.2	122.5
	Br^-	<5.0	<5.0	12.1	<0.3	<0.3	2.0
	NO_3^-	85.4	152.5	265.8	10.8	23.8	50.2
	SO_4^{2-}	204	297	554	32.4	69.9	132.5

	$C_2O_4^{2-}$	<18.0	<18.0	20.8	<1.2	0.2	2.7
	Na^+	55.4	110.7	237.9	10.9	20.1	52.4
	NH_4^+	10.6	12.4	16.6	1.3	2.5	5.9
	K^+	8.0	15.4	23.5	0.8	2.0	3.9
	Mg^{2+}	22.3	43.3	77.4	2.2	7.6	13.3
	Ca^{2+}	<133.1	193.1	409.2	<9.1	14.6	51.5
pH Analyzer	H^+	1.39	4.25	6.97	0.25	0.88	1.87
	(pH)	(5.16)	(5.37)	(5.86)	n/a	n/a	n/a
ICP-MS	Mg	18.2	28.6	67.6	3.0	6.5	14.5
	Al	<3.2	7.2	19.2	<0.2	1.4	3.3
	V	0.006	0.012	0.086	0.002	0.003	0.014
	Mn	0.23	0.64	1.14	0.06	0.10	0.20
	Fe	3.6	10.8	29.1	0.5	2.0	3.9
	Co	<0.002	0.004	0.011	<0.0002	0.0007	0.0015
	Cu	<0.02	0.05	0.28	0.001	0.010	0.053
	As	0.007	0.044	0.071	0.002	0.006	0.013
	Se	0.010	0.024	0.058	0.002	0.004	0.010
	Sb	0.004	0.010	0.018	0.001	0.002	0.004
	Tl	<0.0001	0.0001	0.0004	$<7.2\times10^{-6}$	15.6×10^{-6}	54.0×10^{-6}
	Pb	0.05	0.25	0.41	0.012	0.039	0.086

Notes: MSA = methanesulphonate; ACE = acetate; PRP = propionate; FOR = formate, $C_2O_4^{2-}$ = oxalate; NH_4^+ = ammonium. < # indicates measurement is below MDL.


Black Carbon
20
10
0
MSA
100
50
0
Formate
600
400
200
0
Sea Salt:
Na⁺
Cl⁻
6000
4000
2000
0
NSS-SO₄²⁻
10000
5000
0
NO₃⁻
1500
1000
500
0
NSS-K⁺
100
50
0
Crustal Metals:
Insoluble Al
Insoluble Fe
600
400
200
0
Snow Mixing Ratio (ppb)
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
2014 to 2015 Winter Season

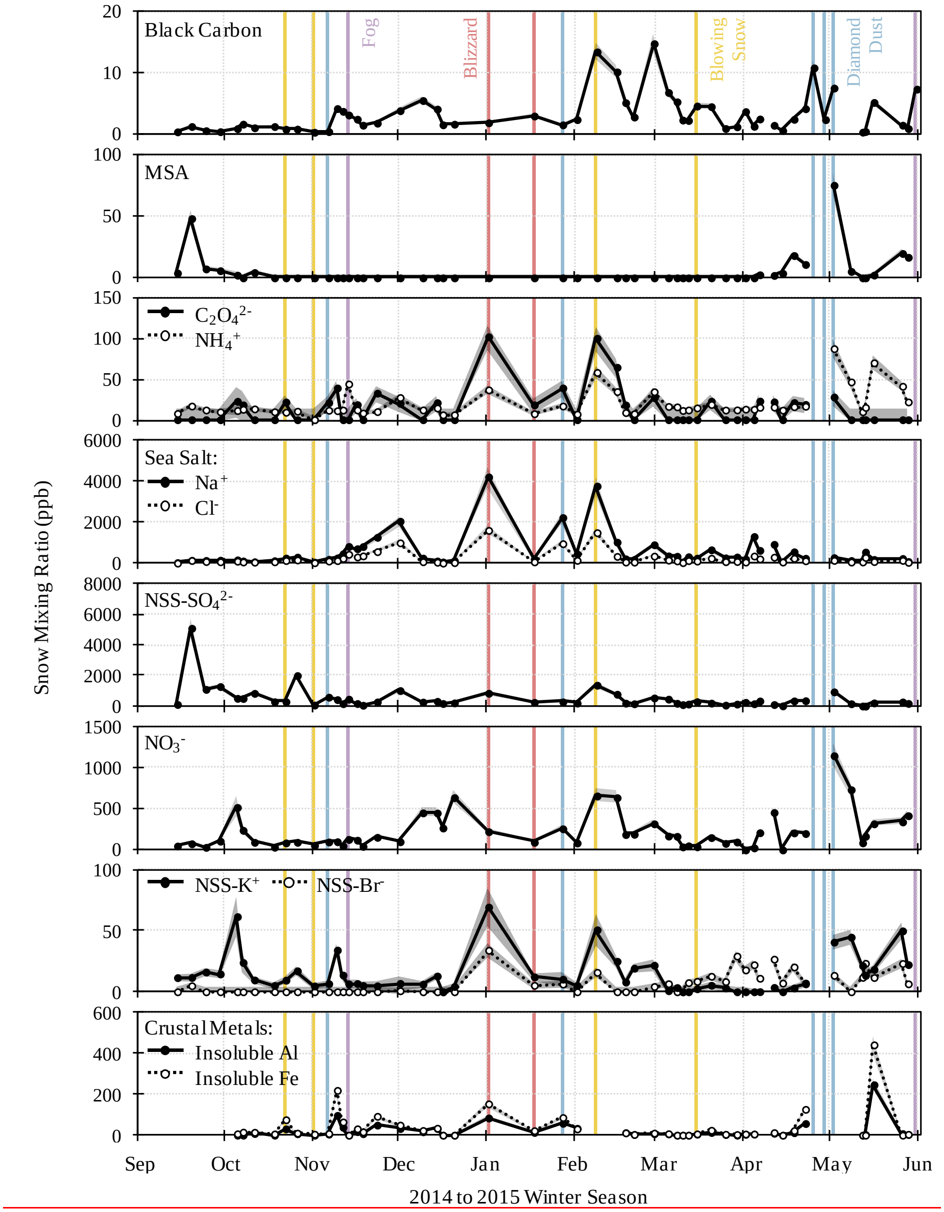

Black Carbon
Fog
Blizzard
Blowing Snow
Diamond Dust
MSA
$C_2O_4^{2-}$
NH_4^+
Sea Salt:
Na^+
Cl^-
NSS-SO_4^{2-}
NO_3^-
NSS-K^+
NSS-Br^-
Crustal Metals:
Insoluble Al
Insoluble Fe
20
10
0
100
50
0
150
100
50
0
6000
4000
2000
0
8000
6000
4000
2000
0
1500
1000
500
0
100
50
0
600
400
200
0
Snow Mixing Ratio (ppb)
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
2014 to 2015 Winter Season

Figure 1: Measured snow mixing ratio (line) and uncertainty (shaded area) of key analytes over 2014 to 2015 campaign.

Comment [KM etal26]: Figure 1 updated to show unusual weather events

A review of existing Arctic snow measurements found the measured median mixing ratios to fall within expected ranges (see supplemental Table S7 for details); however, it should be noted that the referred data represent a variety of collection and analysis techniques. In general, measurements of this campaign showed salt species and non-crustal metals to be at the lower end of the typical range while SO_4^{2-} and NO_3^- were at the higher end. A limited number of seasonal snow collection campaigns were available for comparison of the observed seasonal trend in analytes. The winter peak in BC was similar to that observed by Davidson et al. (1993); however, spring values observed in this campaign were higher than previously seen. The observed seasonal trend in major ions was generally consistent with existing literature (Davidson et al. 1993; Toom-Sauntry and Barrie, 2002). Specifically, a winter peak in sea salt, fall/spring peaks in MSA, and a winter peak in NO_3^- are all typical. However, the fall peak observed in the NSS-SO_4^{2-} mixing ratio and spring peak in NO_3^- were unlike seasonal trends observed previously (Davidson et al. 1993; Toom-Sauntry and Barrie, 2002). Unusual weather events, as noted by the operators, are highlighted in Figure 1; however, no obvious relationship was observed with snow measurements, with the exception of blizzard and high wind conditions in January and February which were associated with elevated mixing ratios for several chemical species. Atmospheric measurements are provided in the supplemental Table S7. As observed for snow, most atmospheric analytes experienced a winter high. The fall/spring peaks in MSA and notable fall peak in SO_4^{2-} persisted in both snow and atmospheric measurements.

Comment [KM etal27]: Expended as per Referee #1 comment

3.2 Factors Influencing Snow Scavenging and Deposition

3.2.1 Effective Deposition Velocity

Comment [KM etal28]: Description of effective deposition velocity revised to provide better clarity

As discussed above, the collected snow samples provide information on the total deposition of material to the surface over a given time and area. In order to elucidate the mechanisms controlling this bulk deposition, a simplistic model for flux, Eq. (1), was ~~used~~adopted to describe the measured deposition:

$$F_{S,total}{}^{ij} = C_A{}^{ij}\, v_{d,eff}{}^{ij}\ , \tag{1}$$

where $F_{S,total}{}^{ij}$ is the flux deposited to snow of the j^th^ analyte over the i^th^ period; $C_A{}^{ij}$ is the arithmetic average atmospheric concentration; and $v_{d,eff}{}^{ij}$ is the effective deposition velocity.

The measured snow flux ($F_{S,total}$) represents the total deposition by wet and dry mechanisms. Thus, the effective deposition velocity ($v_{d,eff}$) encompasses the variety of aerosol and meteorological properties controlling deposition efficiency and the relative importance of each deposition pathway: dry, wet in-cloud, and wet below-cloud scavenging. ~~The~~ This effective velocity is akin to a typical deposition velocity; however, it encapsulates the bulk movement of material by combining the dry deposition velocity and the wet deposition efficiency as an equivalent velocity. Thus, this parameter can be used to provide a holistic view of Arctic deposition. Use of the effective deposition velocity also avoids the uncertainties of estimating the split between dry and wet deposited mass. A caveat to this analysis is that the three deposition mechanisms relate to different atmospheric concentrations, a gradient which is not necessarily captured when the ground-level atmospheric concentration (C_A) is used to calculate the effective deposition velocity: dry deposition affects the lower atmosphere, in-cloud scavenging the cloud layer, and below-cloud scavenging the full below-cloud atmospheric column. ~~So, the calculated velocities have an intrinsic variability dependent on the vertical atmospheric profile of each analyte.~~ Previous observations of vertical profiles in the Arctic have shown ~~a great degree of~~notable variability with altitude~~, but typically within the below cloud layer (the lower 2-4 km) atmospheric concentrations are more consistent~~ (Hansen and Rosen, 1984; Leaitch et al., 1989; Spackman et al., 2010; Brock et al., 2011; Sharma et al., 2013). ~~As well, in NETCARE aircraft measurements yet to be published, it was shown through SP2 and aerosol mass spectrometry measurements of aerosol composition from the ground to 3 km altitude during April, 2015 that little vertical variability was apparent in aerosol BC, SO~~$_4^{2-}$~~, NO~~$_3^-$~~, and ammonium (NH~~$_4^+$~~). Thus, the use of ground level measurements was considered acceptable. An overview of measured atmospheric concentrations is provided in the supplemental (Table S8).~~So, the calculated effective velocity includes an intrinsic variability dependent on the vertical atmospheric profile of each analyte.

Effective deposition velocities were calculated for chemical species measured in both snow (SP2 and IC) and atmospheric (SP2 and Hi-Vol) samples. Figure 2 shows effective deposition velocities calculated as the ratio of total summed snow flux and average atmospheric concentration measured over the same period. Both a six-day resolution, as per the Hi-Vol sampling frequency, and monthly resolution are provided. The calculated effective deposition velocities ranged from 0.001 to 10 cm/s (0 to 16 cm/s with uncertainty). Episodic and monthly peaks are observed in Figure 2 for each analyte. The variance in deposition observed by composition and temporally is discussed below.

Comment [KM etal29]: Removed as per Referee #1 comment

Comment [KM etal30]: Removed as per Referee #1 and #2 comments

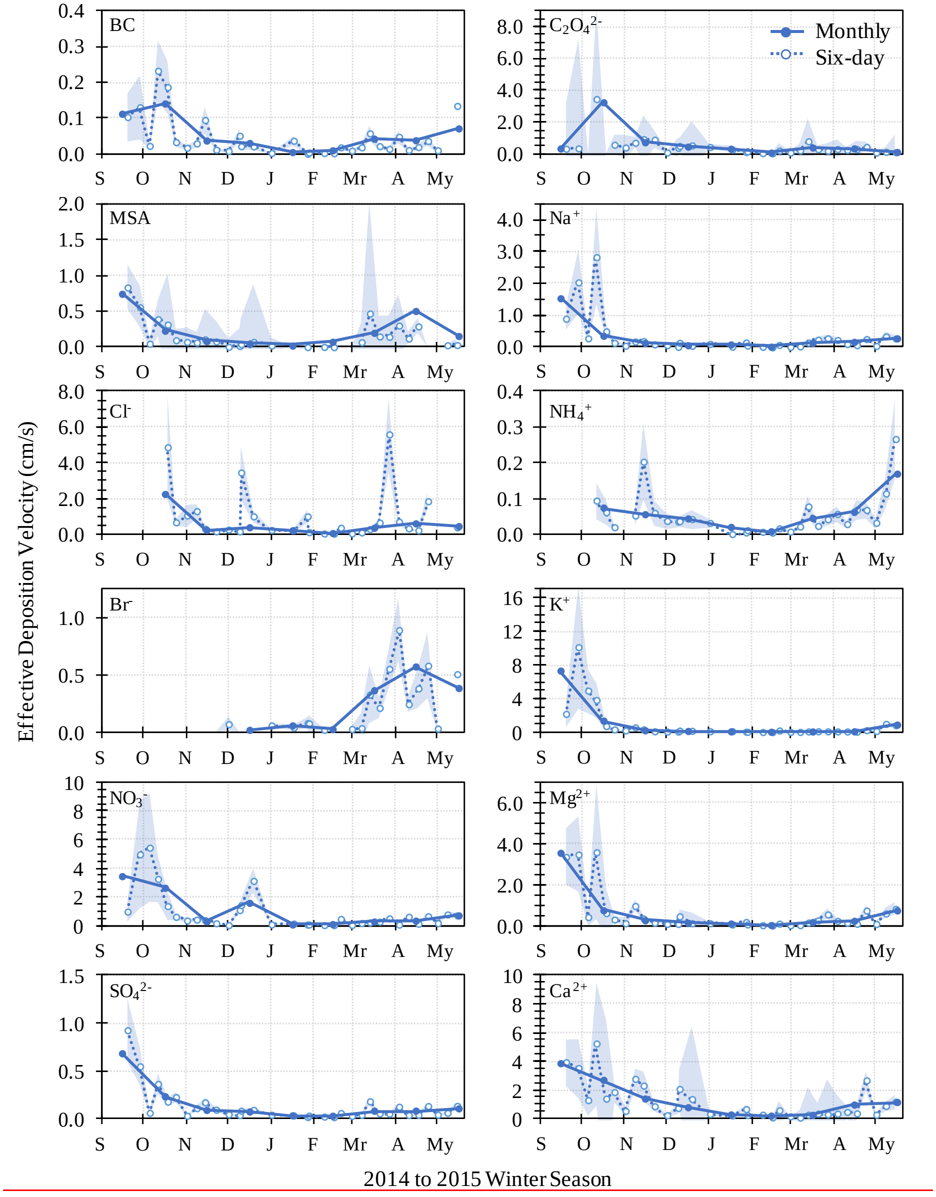

Effective Deposition Velocity (cm/s)
BC
0.4
0.3
0.2
0.1
0.0
$C_2O_4^{2-}$
8.0
6.0
4.0
2.0
0.0
Monthly
Six-day
MSA
2.0
1.5
1.0
0.5
0.0
Na^+
4.0
3.0
2.0
1.0
0.0
Cl^-
8.0
6.0
4.0
2.0
0.0
NH_4^+
0.4
0.3
0.2
0.1
0.0
Br^-
1.0
0.5
0.0
K^+
16
12
8
4
0
NO_3^-
10
8
6
4
2
0
Mg^{2+}
6.0
4.0
2.0
0.0
SO_4^{2-}
1.5
1.0
0.5
0.0
Ca^{2+}
10
8
6
4
2
0
S
O
N
D
J
F
Mr
A
My
2014 to 2015 Winter Season

Figure 2: Effective deposition velocity at monthly (solid) and approximately 6-day (dashed) frequencies with 6-day uncertainties (shaded area). Missing values indicate periods with snow and/or atmospheric measurements below detection limits.

3.2.2 Variation in Deposition by Composition

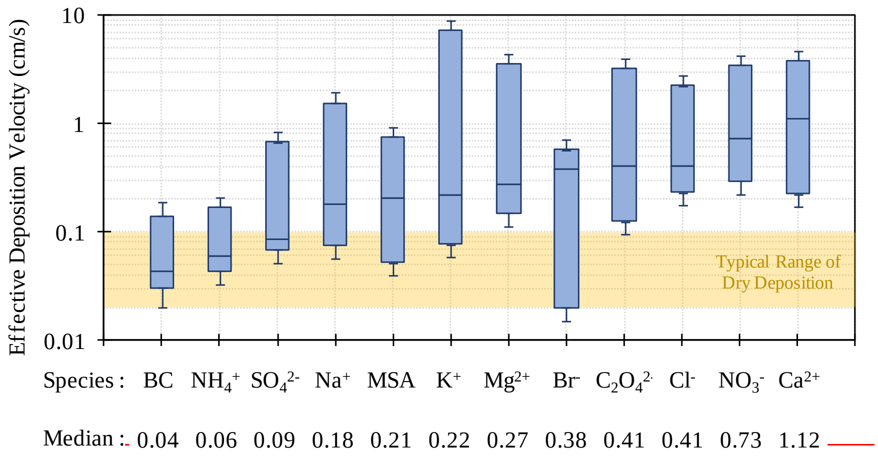
~~The ratio of monthly total snow flux to monthly averaged ground level atmospheric concentrations was used for the calculation of effective deposition velocities. The use of monthly values allowed for intra-monthly variability in deposition conditions, such as snow type and snow/air interface properties which were not explicitly monitored and would complicate analysis of deposition over individual snowfall events. Thus, the range of calculated effective deposition velocities of an analyte describes their general deposition regime, capturing the impacts of any parameters which led to seasonal changes in the predominant deposition mechanisms directly or through changes in aerosol aging.~~

Monthly effective deposition velocities were used to contrast deposition mechanisms by aerosol composition. A monthly resolution provides insight into the general deposition regime of each analyte, highlighting the impact of bulk deposition characteristics rather than event-specific variability. The variability between aerosol of different composition and the influences of seasonal changes within the Arctic system are simpler to identify without the interference of variability between event-specific conditions. A monthly analysis also ~~provides for better~~facilitates future ~~comparisons~~comparison with modelled results which ~~would~~may not replicate individual events.

~~The calculated monthly effective deposition velocities are summarized in Figure 2 for analytes measured both in fresh snow (via SP2 and IC) as well as in the ground level atmosphere (via SP2 and Hi-Vol filters). Median effective deposition velocities ranged from 0.04 to 1.1 cm/s. January and February velocities were excluded from median calculation~~ January and February, 2015, were excluded from the monthly analysis because blizzard and high wind conditions were believed to have caused significant losses of snow from the snow tables during these months (based on operator reports~~ and larger snow depths measured at local meteorological stations~~), which would lead to underestimation of these snow flux ~~for these months. Since wet deposition is a function of precipitation volume, the~~values. The effective deposition velocity is ~~comparable only~~best suited to analysis across periods of equal ~~total precipitated volume.~~length and precipitation volume, since both of these parameters are inherently included when the wet deposition efficiency is converted to an equivalent deposition velocity. With the exception of January and February~~, 2015~~, the total monthly snow precipitation over the campaign was relatively constant, with a relative standard deviation of 20%.~~ Error bars in Figure 2 describe the combined uncertainty of the snow and atmospheric measurements.~~

Comment [KM etal31]: Figure 2 moved from supplemental to manuscript and 6-day resolution added as per Referee #1 and #2 comments

Comment [KM etal32]: Section rearranged and revised to improve flow with added Figure 2 and discussion



~~**Figure 2: Effective deposition velocities. Columns show the calculated minimum, median, and maximum monthly effective deposition velocities over the sampling campaign, excluding January and February, 2015. Error bars show uncertainty of deposition velocities. Typical range of dry deposition velocity for accumulation mode particles to snow by others (Davidson et al., 1987; Petroff and Zhang, 2010).**~~

~~The range of calculated effective deposition velocities was compared to the expected range of dry deposition velocities for typical accumulation mode Arctic particles, 0.02 to 0.10 cm/s (Davidson et al., 1987; Petroff and Zhang, 2010), as highlighted in Figure 2. The calculated effective velocities fell within or above the dry deposition range, indicating dry deposition may be the dominant deposition mechanism in some measurements while others show enhanced deposition with an increased influence of wet deposition processes.~~

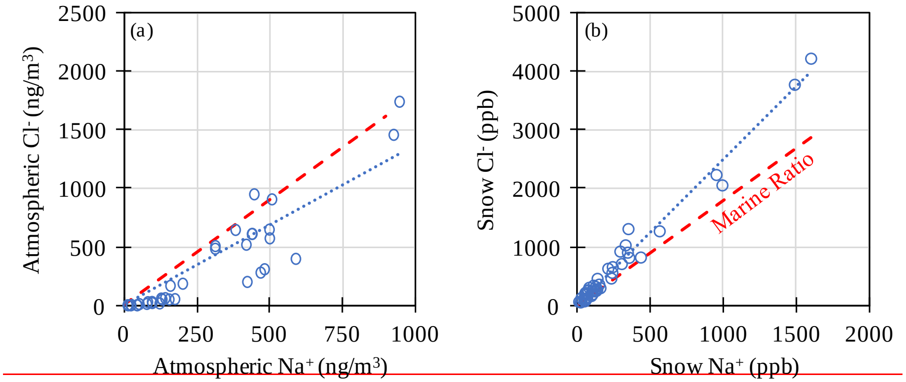
~~3.2.2 Variation in Deposition by Composition~~

~~Deposition efficiency is dependent on the properties of the aerosol being deposited.~~ Figure 3 shows that the typical deposition characteristics varied by analyte, with median effective deposition velocities ranging from 0.03 to 1.1 cm/s; however, error bars describing the combined uncertainty of the snow and atmospheric measurements show that the range of calculated effective deposition velocities of each analyte have considerable overlap. The calculated monthly effective deposition velocities showed a relative standard deviation of 60 to 150% across the measured analytes, while measurement-based uncertainty was estimated as only ±35%, indicating a significant impact of aerosol state or properties on deposition. ~~This variability could be the result of variations in aerosol phase and/or particle size, shape, and cloud nucleation affinity. The only size-resolved speciated analysis available to this study was SP2; however, the mass diameters estimated by SP2 do not provide information on the aerodynamic diameter which is of greater concern in deposition processes. Furthermore, it could not be known if BC size distribution in the snow samples was maintained over sample melt and sonication prior to analysis. Without additional information, the impact of size and shape on deposition could not be inferred from this study~~

~~beyond simple deductions based on the typical particle sizes associated with aerosol types. Similarly, due to a lack of information, the possible impact of particle coating was not addressed. The observed differences in deposition are therefore primarily discussed in the context of phase state and cloud nucleation affinity.~~

~~Due to the nature of the Hi-Vol analysis, the measured atmospheric concentrations include only the particle phase ambient species; however, snow can scavenge both the particle and gas phases, and thus snow samples provide a composite measurement of both. The measurement of sea salt species was used as a case study to illustrate the impact of particle/gas-phase partitioning. The two dominant components of sea salt, Na and Cl, were measured both in snow samples (IC) and in the atmosphere (Hi-Vol). Previous studies have found Na and Cl observed within the Arctic to be predominantly marine in origin (Sirois and Barrie, 1999; Nguyen et al., 2013). This marine origin is supported by the excellent correlation of Na and Cl ions measured in snow (Pearson's correlation of 0.99), indicating a common source. The ratio of Na and Cl in sea salt is well established and consistent globally (Pytkowicz and Kester, 1971). So, the measured relationships of these chemical species in the atmosphere and snow were compared to the expected marine ratio (Figure 3).~~

Comment [KM etal33]: Discussion of Cl enhancement reduced as per Referee #1 comment



~~**Figure 3: Atmospheric (a) and snow (b) sea salt measurements. The marine ratio of Cl$^-$/Na$^+$, shown in red (1.795 mass/mass), is compared to the measured average ratios, shown in blue as the line of best fit, for atmospheric (slope=1.36, correlation=0.92) and snow measurements (slope=2.49, correlation=0.99).**~~

~~It was observed that while atmospheric particulate monitoring showed a deficit in Cl, snow samples showed an enhancement in Cl relative its marine ratio with Na. This discrepancy may be explained by partitioning of Cl from the particle to the gas phase, and subsequent gas-phase scavenging by snow. It has been suggested that Cl within Arctic aerosol will partition to the gas phase during the winter, likely in the form of HCl via acid displacement reactions; however, there is no similar evidence for Na being involved in analogous chemistry (Toom-Sauntry and Barrie, 2002). The gas-phase portion of Cl would not be captured by atmospheric particulate monitoring, causing a perceived deficit and reducing the correlation of Na and Cl if the gas-phase partitioning were non-linear. In contrast, gas-phase Cl deposited to the snowpack would be measured during snow analysis, leading to an increased Cl/Na ratio and an improved agreement between Cl and Na. The proportion of Cl in the atmosphere which partitioned to the gas phase was estimated from the observed atmospheric deficit below the marine ratio to~~

~~be approximately 24% by mass on average over the 2014-15 winter season (assuming a common marine origin of Na and Cl and that Na remains fully in the particle phase). In addition, the enhancement of Cl in snow above the marine ratio demonstrates that gas-phase Cl was preferentially deposited to the snow over the particle phase. Snow Cl scavenged from the particle phase was estimated from snow Na using the observed atmospheric Cl/Na ratio (1.36 mass/mass) and the remaining Cl in snow was considered to be scavenged from the gas phase. Based on these estimated gas and particle-phase proportions in the snow and atmosphere, median effective deposition velocities were calculated as 0.16 and 0.40 cm/s for the particle and gas phases, respectively. Comparison of these velocities indicates an 86% enhancement in gas-phase deposition relative to that of the particle phase.~~

~~The effective deposition velocities provided in Figure 2 showed BC to have the lowest median velocity. The velocities of NH_4, SO_4, Na, K, Mg, C_2O_4, and Ca showed enhancement relative to BC, though statistical significance could be shown only for Ca^{2+} using the ANOVA test (p-value 0.008) due to the low number of samples. Particles containing these analytes~~

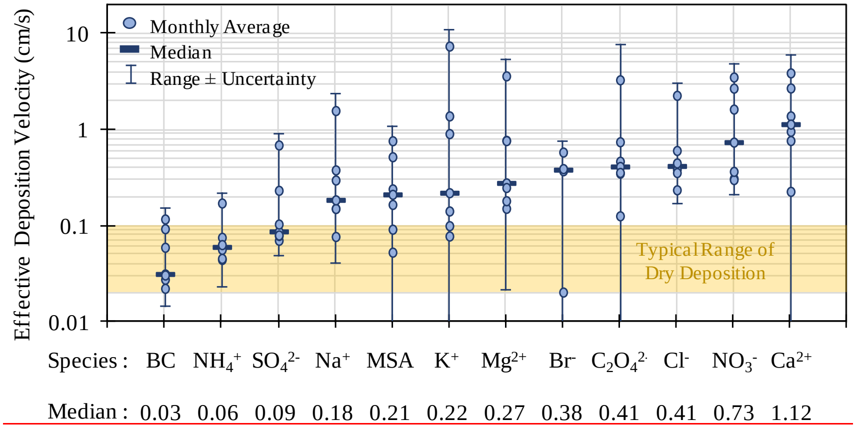


Figure 3: Monthly effective deposition velocities by composition (points, excluding January and February). The median of each analyte (bar) and full range with uncertainty (error bar) are also shown. Also shown is the typical range of dry deposition velocity for accumulation mode particles to snow by others (Davidson et al., 1987; Petroff and Zhang, 2010).

Comment [KM etal34]: Figure 3 (previously Figure 2) revised as per Referee #2 comment

The variability observed between analytes may be the result of variations in aerosol properties. First, the measured chemical species differ in terms of dominant phase: BC, NH_4^+, SO_4^{2-}, Na, K, Mg, $C_2O_4^{2-}$, and Ca are typically observed predominantly in the particle phase, while MSA, Br, Cl, and NO_3^- and their associated precursors can have appreciable gas-phase portions (Barrie and Hoff, 1985). In general, analytes considered to be dominantly particle-based were seen to exhibit lower deposition velocities than those which may have existed as gases. This observation is supported by a detailed study of sea salt species. The Cl in salt particles has been previously observed to partition to the gas phase over winter months (e.g., Barrie and Hoff, 1985; Toom-Sauntry and Barrie, 2002; Quinn et al., 2009); thus, Arctic salt particles often show a Cl deficit while gaseous Cl shows enhancement. Such a process was corroborated by comparison of the atmospheric Hi-Vol and snow

IC measurements for Na and Cl. Both atmospheric and snow measurements showed high correlation of Na and Cl analytes, 0.92 and 0.99, respectively. Yet, the ratio of Cl/Na differed between measurement mediums with a higher proportion of Cl observed in snow (Cl/Na=2.49 mass/mass) than in atmosphere (Cl/Na=1.36). Compared to the typical marine ratio (Cl/Na=1.795; Pytkowicz and Kester, 1971), the atmosphere showed a deficit in Cl while snow showed enhanced Cl (see supplemental Figure S4). It is expected that the Hi-Vol measurement technique would collect predominantly atmospheric particles, while snow would scavenge both gaseous and particulate aerosol. Thus, the enhanced Cl in snow above that of sea salt indicates that Cl partitioned to the gas phase, that both phases deposited to snow, and that gas-phase Cl was scavenged to snow preferentially. Assuming all Na and Cl originated as sea salt particles, Cl mass in each phase can be estimated in the atmosphere and snow. Based on these estimated proportions in the snow and atmosphere, median effective deposition velocities were calculated as 0.16 and 0.40 cm/s for the particle and gas phases, respectively. Comparison of these velocities indicates an 86% enhancement in gas-phase deposition relative to that of the particle phase. Thus, gaseous scavenging may contribute to the enhanced bulk deposition observed in MSA, Br, Cl, and NO_3^-.

Particle nucleation affinity may also be a significant contributor to the observed differences in bulk deposition. The lowest velocities were observed for BC, NH_4^+, and SO_4^{2-}, which largely fell within the typical range of deposition velocities seen for dry deposition: 0.02 to 0.10 cm/s for typical accumulation mode Arctic particles (Davidson et al., 1987; Petroff and Zhang, 2010), as highlighted in Figure 3. In contrast, the monthly velocities of other particle-dominated chemical species, Na, K, Mg, $C_2O_4^{2-}$, and Ca all fell above the typical dry deposition range. Particles containing these analytes, as well as NH_4^+ and SO_4^{2-}, have been previously suggested to act as better precipitation nuclei than BC (e.g., Zobrist et al., 2006; Hoose and Möhler, 2012; Farmer, Cappa, and Kreidenweis, 2015)~~,~~; thus, their enhanced velocities might be attributed to either enhanced scavenging via cloud formation or in-cloud scavenging. Thus, dry deposition may be the dominant deposition mechanism in some measurements while others show enhanced deposition which likely reflects an increased contribution of wet deposition processes. The observed difference in deposition velocities also implies that BC/SO_4^{2-}/NH_4^+-containing particles are to a significant extent externally mixed from these other constituents.

Furthermore, salt and crustal particles may experience enhanced deposition since they typically consist of coarser particles than BC, SO_4^{2-}, and NH_4^+. Specifically, coarse mode particles can exhibit dry deposition velocities to snow up to 0.6 cm/s and below-cloud scavenging efficiencies enhanced over accumulation mode particles by a factor of 10 (Zhang and Vet, 2006; Petroff and Zhang, 2010).~~ The observed difference in deposition velocities also implies that BC-containing particles are to a significant extent externally mixed from these other constituents. Gas phase deposition to snow is suggested to contribute to the observed enhanced velocities of methanesulphonate (MSA), Br, Cl, and NO_3 relative to BC, either due to gas phase emissions or gas phase partitioning during aerosol aging followed by subsequent deposition.~~ The enhancement of Ca above other crustal-related analytes is unexpected. This cannot be satisfactorily explained without further study; however, the phenomenon may be connected to the dissimilar sources of Ca-rich mineral dust to that of other crustal species suggested by other studies (Banta et al., 2008). In addition to aerosol phase, nucleation affinity and size as discussed above, particle

Comment [KM etal35]: Discussion of Ca enhancement moved up as per Referee #1 comment coating could also impact the scavenging and deposition process. However, the potential influence of coatings on the observed velocities cannot be addressed with the available information.

3.2.3 Temporal Variability of Deposition

Shared temporal trends in effective deposition velocity can be observed in Figure 2. A general trend of heightened deposition in the fall and spring can be observed across all analytes. In particular, BC, Na, Mg, and Ca can be seen to share a similar seasonal and episodic trend, with Pearson's correlation coefficients of 0.7 to 0.9 (comparing six-day resolution, excluding January and February, 2015, p-values <0.001). Episodic peaks in Mg and Ca also show some similarity to SO_4^{2-} (correlation of 0.70-0.85, p-value <0.001). The trend of NH_4^+ is more difficult to distinguish as September measurements were below detection limit; however fall and spring peaks are suggested. A more pronounced fall peak was observed in SO_4^{2-}, Na, K, and Cl, though their episodic peaks differ. Although MSA is distinguished by a spring peak, MSA and SO_4^{2-} share similar episodic peaks with a six-day correlation of 0.86 (p-value <0.001). The seasonal trends of Br, $C_2O_4^{2-}$, and NO_3^- are more distinct: Br exhibits a broad spring peak, $C_2O_4^{2-}$ a short October peak, and NO_3^- a broad fall/winter peak. Episodic $C_2O_4^{2-}$ showed moderate correlation with BC, Na, Mg, and Ca (coefficient=0.5-0.7, p-value<0.02) and NO_3^- episodes showed correlation with K (coefficient=0.83, p-value<0.001). There are some peak events shared across several analytes, for example, an early October peak is observed in most chemical species. While the differing magnitudes of effective deposition velocities observed across analytes implies separate scavenging and deposition, these shared temporal trends indicate that the externally mixed particles and gaseous chemical species are subject to similar temporal influences controlling deposition.

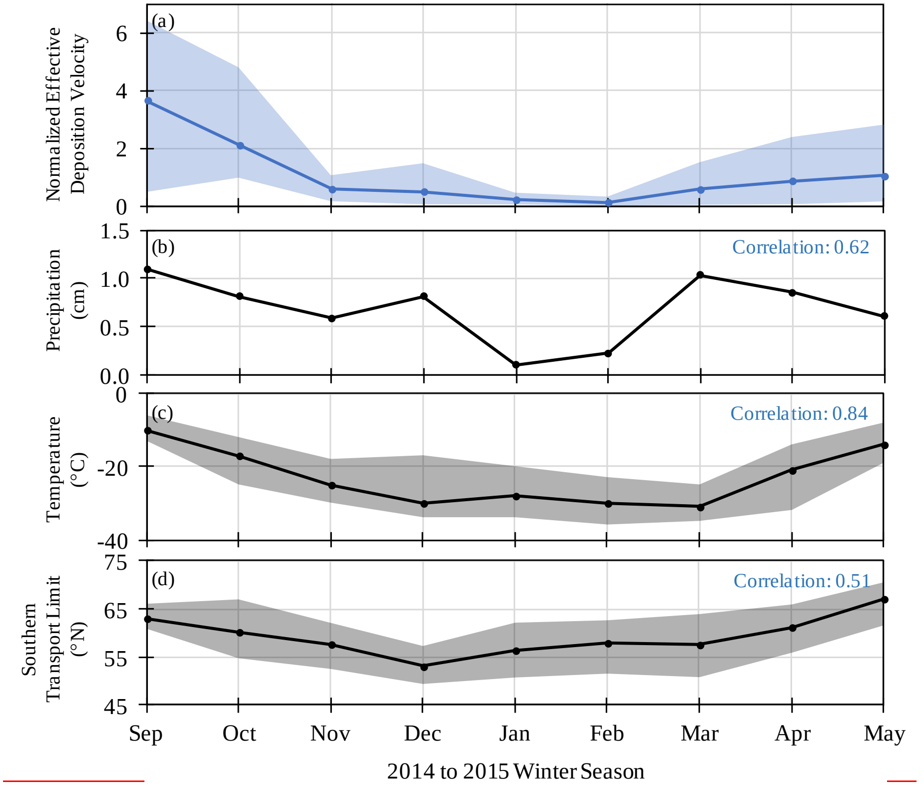
Comment [KM etal36]: Discussion of analyte individual trends included since plot provided above

Several factors controlling deposition experience seasonal variations, which may have contributed to the observed inter-monthly variability.~~ Across the campaign months, a relative standard deviation of 60 to 180% was observed in deposition velocities. Figure 4 shows the range of effective deposition velocities normalized by their associated campaign average for all measured chemical species over the sampling campaign as well as the average seasonal trend (the seasonal trends of individual analytes are provided in the supplemental Figure S3). In general, higher velocities were observed in the fall and spring. The deposition velocities for January and February are low and may be underestimated due to the presumed loss of snow from the snow tables during these months.~~

~~Three~~ Six properties of the Arctic system with seasonal trends were considered as possible influences on the observed velocity trend: precipitation, temperature, ~~and~~ mixing height, cloud height, dominant aerosol source region, and sunlight availability, as shown in Figure 4. The precipitated snow-water equivalent depth was calculated from the snow mass and table area of each sample~~ and temperature monitored at local meteorological stations over the campaign. The dominant aerosol source of each month was described using the southern limit to transport, calculated from the FLEXPART results as the latitude which encircles 98% of the 10-day transport source area and presented as a range based on initialization altitude (100 m, 500 m, 1 km, and 2km above Alert)~~. Temperature was monitored at local ground-level meteorological stations over the campaign (supplemental Table S9) and sunlight estimated from location and time of year. The dominant aerosol source

Comment [KM etal37]: Additional meteorological parameters considered as per Referee #1 comment of each month was described using the southern limit to transport and mixing/cloud heights were estimated from radiosonde data, as described above.

Comment [KM etal38]: Description of transportation limit moved to methodology as per Referee #2 comment



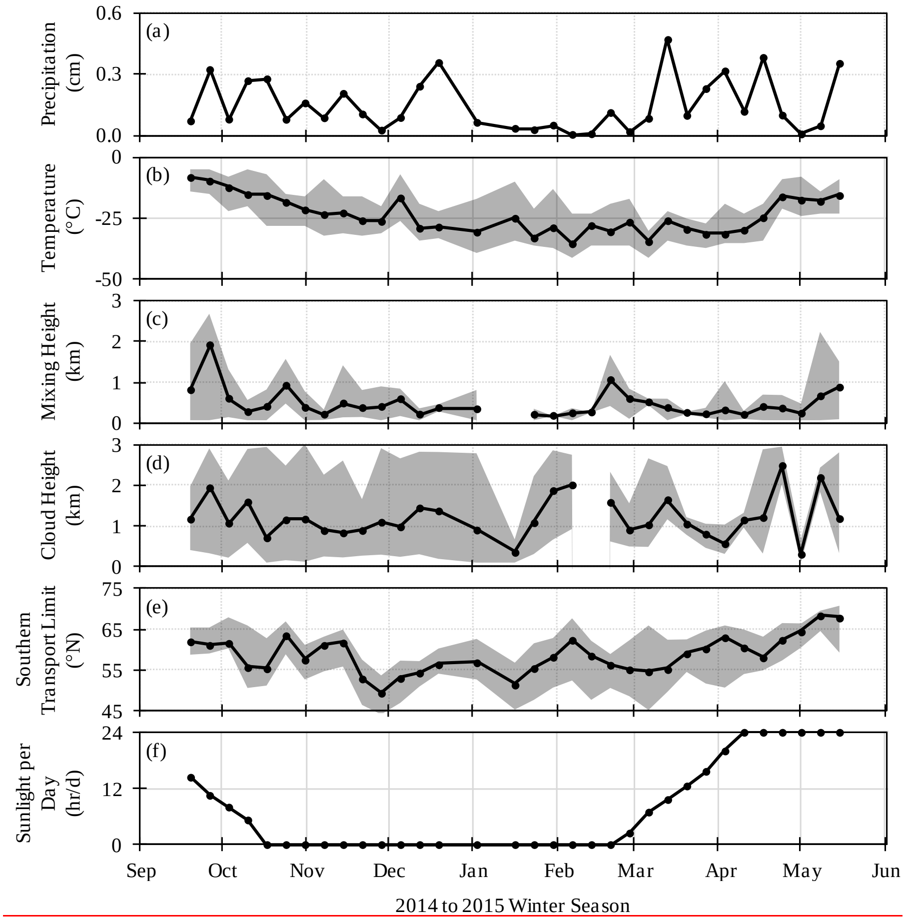


Figure 4: Seasonal variation in ~~deposition velocity (a),~~ precipitation (~~b~~a), temperature (b), mixing height (c), ~~and~~ cloud height (d), transport (~~d). For velocity~~e), and sunlight (f). Precipitation and ~~temperature, the shaded areas show the range of observations over each month and the lines show~~ sunlight are presented as the average ~~monthly value. For precipitation, the total monthly depth is shown. For~~ per snow sample collection period. Temperature, mixing/cloud height, and southern transport limit are presented as the average for each collection period (line) along with the full range (shaded area).~~, the shaded area shows the range of average latitudes across the modelled receptor altitudes and the line shows the average transport limit. Correlations with the average normalized effective deposition velocity are provided.~~

Temperature, transport, ~~The~~and sunlight can be seen to follow similar seasonal ~~pattern~~trends with fall/spring peaks. Precipitation, mixing height, and cloud height exhibit episodic peaks and a less significant seasonal trend (relative standard deviation intra-monthly was a factor of ~~the average~~ 1.5 to 2 times higher than inter-monthly, whereas these values were approximately equal for temperature, transport, and sunlight). When compared to effective deposition ~~velocity showed~~

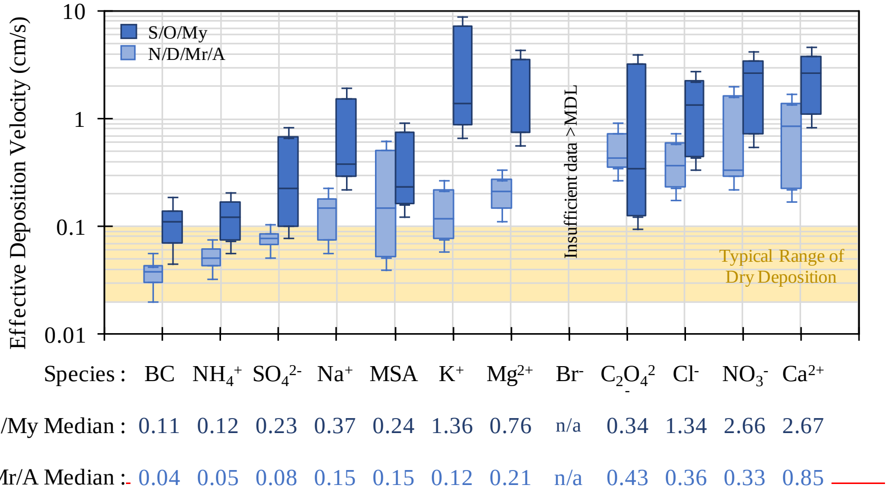
Comment [KM etal39]: Figure 4 updated to include additional meteorological parameters. Normalized velocity removed since individual trends provided above.

velocities, BC, SO_4^{2-}, Na, Mg, NO_3^-, and Ca show better ~~agreement~~correlation with temperature than the ~~seasonal trend~~other meteorological conditions shown in ~~temperature than with that of precipitation depth or transport limit~~Figure 4, with Pearson's correlation coefficients ~~of 0.8, 0.6, and 0.5~~above 0.5 (excluding January and February, 2015, p-value <0.02). Specifically, SO_4^{2-}, K, Mg, and Ca had high correlation coefficients with temperature of 0.6-0.7 (p-values <0.002). Medium to high correlations were observed between mixing height and SO_4^{2-}, Na, K, Mg, and NO_3^-, with coefficients of 0.4-0.7 (highest correlation for K at 0.76) and p-values below 0.05. Bromide deposition showed high correlation with sunlight (coefficient: 0.6, p-value: 0.001). In contrast, NH_4^+ and MSA only showed weak correlation with the described meteorological parameters (maximum coefficients of about 0.4 with transport and mixing height, respectively~~ (0.80, 0.52, and 0.44 if January and February are excluded) with p-values of 0.005, 0.08, and 0.16, respectively~~). In contrast, $C_2O_4^{2-}$ and Cl did not show strong correlations with any of the described meteorological parameters (coefficients below 0.2). Overall, temperature showed the best correlation with deposition velocities for most analytes, followed by mixing height. Thus, changes in temperature may be linked to seasonal changes in the dominant scavenging mechanism of several analyzed species. Specifically, it is hypothesized that the increased presence of mixed-phase clouds with warmer temperatures may have enhanced wet deposition via in-cloud scavenging due to CCN activity~~.~~ for those analytes expected to exist predominantly in the particle phase: BC, NH_4^+, SO_4^{2-}, Na, K, Mg, NO_3^-, and Ca.

Comment [KM etal40]: Discussion of temporal variability revised to include additional meteorological parameters and higher resolution data

The effective deposition velocities for warmer and colder months were separated using a -20 °C cut-off between ice-cloud dominated periods, November to April (N/D/Mr/A), and months with a significant potential for mixed-phase clouds, September, October, and May (S/O/My). Radiosonde observations show temperatures at typical cloud heights usually above -20 °C in S/O/My and below -20 °C in N/D/Mr/A, supporting the mixed-phase cloud hypothesis. Comparison of the effective deposition velocities delineated by these periods minimized the influence of precipitation volume as it was relatively constant: an average of 12 mm/month in S/O/My and 18 mm/month in N/D/Mr/A. However, the influence of aerosol source may differ by period given their distinct source profiles: long-range transport dominated in N/D/Mr/A, and local transport dominated in S/O/My. Figure 5 depicts the range of effective deposition velocities calculated for each analyte over these two periods (again excluding January and February). Bromide was excluded from this analysis since it was below detection limit in the snow and/or atmospheric measurements from September to November.

Comment [KM etal41]: Additional support available from added meteorological analysis



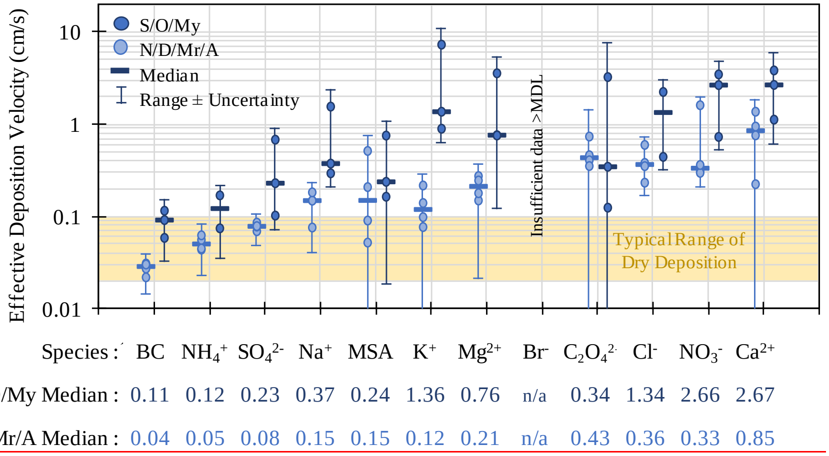


Figure 5: Effective deposition velocities split by season. The effective deposition velocities are separated into two time periods: warmer months S/O/My = September/October/May, and colder months N/D/Mr/A = November/December/March/April.

Comment [KM etal42]: Figure 5 update as per Referee #2 comment

With the exception of $C_2O_4^{2-}$, all analytes showed a larger median effective deposition velocity for the warmer S/O/My months than the colder N/D/Mr/A months. Although insufficient data are available to confirm the statistical significance for each individual analyte, the combined normalized dataset of velocities showed significant enhancement during S/O/My using the ANOVA test (p-value 4.9×10^{-8}). Specifically, marked enhancement was seen for BC, NH_4^+, SO_4^{2-}, Na, K, and Mg. The cold-month deposition of these analytes can largely be described by dry deposition alone with velocities below 0.1 cm/s for analytes expected to be dominated by accumulation mode particles and 0.6 cm/s for those expected to include significant coarse-mode mass; however, their warm-month effective deposition velocities were a factor of 2 to 12 higher.

The unexpected discrepancy in the deposition of Ca and Mg given their typically similar origins, as discussed above, was also observed when comparing median warm and cold month periods. Both Mg and Ca are common to sea salt and crustal origins but their non-sea salt (NSS) portions can be estimated based on typical sea salt ratios with Na (Pytkowicz and Kester, 1971). The NSS-Mg and NSS-Ca showed similar behaviour over the warm months, with average velocities of 2.4 and 2.6 cm/s, respectively, but a larger difference in the cold months, with average velocities of 0.4 and 1.0 cm/s, respectively. No explanation of this discrepancy can be supported without further study; however, it appears that Ca and Mg exist as externally mixed Ca-rich and Mg-rich crustal particles which are subject to differing deposition processes, particularly in dry deposition-dominated colder months.

Comment [KM etal43]: Discussion moved and expanded as per Referee #1 comment

~~This suggests that these chemical species~~Thus, the observed effective deposition velocities suggest that most analytes and particularly those expected to exist primarily as particle phase were preferentially scavenged during the warmer S/O/My months, possibly due to the presence of mixed-phase clouds and the associated CCN activation of these chemical species or enhanced below-cloud deposition of those compounds typically associated with larger particles. However, the change in source profile typically experienced during these months along with other seasonal changes in aerosol processing and altitudinal distribution might have also contributed to the observed S/O/My enhancement. In particular, records of volcanic activity show that the Icelandic volcano Bárðarbunga was active August, 2014 through February, 2015 (Global Volcanism Program, retrieved March 2016 from http://volcano.si.edu/), which likely contributed to a shift in the dominant source and scavenging-related properties of SO_4^{2-} over the campaign that would not be representative of a typical year. The overlapping warm/cold-month ranges observed for Cl, MSA, $C_2O_4^{2-}$, and NO_3^- suggest that the deposition of these chemical species was more strongly driven by factors other than nucleation, such as gas-phase partitioning or other aerosol aging processes. For example, enhanced deposition of MSA and Br^- was observed as early as March and April, which could imply that their deposition was impacted by changes in the atmospheric processing of these chemical species during polar sunrise.

~~The enhanced deposition of Ca compared to the other particle phase species is unexpected. Both Mg and Ca are common to sea salt and crustal origins but their non-sea salt (NSS) portions can be estimated based on typical sea salt ratios with Na (Pytkowicz and Kester, 1971). The NSS-Mg and NSS-Ca showed similar behaviour over the warm months, with average velocities of 2.4 and 2.6 cm/s, respectively, but a larger difference in the cold months, with average velocities of 0.4 and 1.0 cm/s, respectively. Assuming a crustal source with internally mixed aerosol these analytes would have been expected to show more similar velocities. No explanation of this discrepancy can be proposed without further study; however, the phenomenon may be connected to the dissimilar sources of Ca rich mineral dust to that of other crustal species suggested by other studies (Banta et al., 2008).~~

4 Conclusions

To help characterize the chemical state of the rapidly changing high Arctic, an intensive campaign of fresh snow sampling at Alert, Nunavut, was completed and snow quantified for a broad suite of analytes. Comparison of these snow measurements with coincident atmospheric measurements allowed estimation of monthly effective deposition velocities describing the total dry and wet deposition in the range of about 0.02 to 8 cm/s. The calculated effective deposition velocities for several measured chemical species resemble those expected for dry deposition alone, suggesting that dry deposition may be the dominant removal mechanism, especially for winter scavenging of BC, NH_4^+, SO_4^{2-}, Na, and K. Enhanced deposition during September, October, and May suggests that wet deposition may increase in importance during these warmer months, possibly due to the presence of mixed-phase clouds and the associated scavenging of crustal, salt, and SO_4^{2-} species as CCN; however, other factors such as changes in the dominant aerosol source profile may also contribute to the observed trend. Comparison of salt species measurements in the Arctic snow and atmosphere suggested that Cl experiences significant gas-phase partitioning and that this gas phase ~~material~~ may be preferentially scavenged. Such gas-phase scavenging may contribute to the enhanced deposition of MSA, Br, Cl, and NO_3^- observed relative to BC, in conjunction with other aerosol processing differences. The low deposition ~~efficiency~~velocity of BC-containing particles is consistent with those particles being externally mixed from more soluble species and having a low cloud nucleation efficiency. Given the rarity of temporally-refined and broadly speciated Arctic snow sampling campaigns, measured deposition magnitudes and insights on deposition mechanisms such as these are valuable for future model validation.

Author Contribution

Organization of the snow collection campaign was le~~a~~d by S. Sharma with the assistance of A. Platt and sample collection by M. Elsasser. Snow SP2 analysis was completed by J. McConnell and N. Chellman, snow IC analysis lead by D. Toom with the assistance of A. Chivulescu, and snow ICP-MS by K. Macdonald with the assistance of Y. Lei. Analysis of radiosonde data was completed by D. Tarasick. Ambient atmospheric monitoring of inorganic aerosols was completed by D. Toom and monitoring of BC by S. Hanna with the assistance of A. Bertram~~ and Richard Leaitch~~. FLEXPART simulations were completed by H. Bozem and D. Kunkel with data analysis assisted by K. Macdonald. Data interpretation was led by K. Macdonald with input and comments by all authors. ~~Dr.~~ G. Evans and J. Abbatt provided oversight for the project, including input on the manuscript.

Comment [KM etal44]: Analysis added as per Referee #1 comment

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

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Comment [KM etal45]: Reference to unpublished work removed as per Referee #1 and #2 comments

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Comment [KM etal46]: References moved to supplemental since methodology n manuscript reduced

Comment [KM etal47]: Removed reference to thesis as per Referee #1 and #2 comments

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