

# 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 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-Saunty 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 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; Leitch 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 the 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  $\pm$  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.