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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Measurement report: Spatial variations in snowpack ionic chemistry and water stable isotopes across Svalbard” *by* Elena Barbaro et al.

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R: In this paper, the authors conducted snow observations on several glaciers in Svalbard in springtime and showed spatial variations of the loads of chemical substances in snowpack and water stable isotopes. The spatial variations influenced by an unique location of Svalbard, which is in the boundary area of sea ice cover, are valuable data to evaluate transportation processes of chemical substances and water vapour surrounding Svalbard. Especially, a spatial variation of Br, which is reported by less common of previous research is very important and suggests release processes of Br from sea ice during sea ice formation. Moreover, the unification of observation methods of snowpack and chemical analyses conducted by several laboratories enhances the reliability of the data. For these reasons, I suggest that this manuscript is worthy of being a publication of ACP as a measurement report. However, I believe that the data currently described in this manuscript are not enough. The authors also observed snow stratigraphy of snowpack and collected snow samples for chemical analyses from each snow layer according to the snow stratigraphy. Nevertheless, only total loads of chemical species in snowpack are reported in the current manuscript. I am strongly proposing that spatial variations of SWE-weighted mean concentrations as well as total load are at least reported in the main content of the manuscript and vertical profiles of stratigraphy of snow pack and concentration of chemical substances and water stable isotopes are reported in the main content of the manuscript or the supplementary materials.

A: We thank the reviewer for the useful comments. While we agree that going into the details of the layer resolution is of interest, we feel that it is out of the scope of this manuscript. In this paper, we present and discuss the spatial and altitudinal loads of different chemical species in the Svalbard Islands. For this reason, we omitted the description of the vertical snowpack profiles for each site and focused the discussion only on the total load, but have now included some figures that show the changes in snowpack density (Fig S4). In snow pits, it is rather difficult to associate a specific layer to a specific period and this makes the interpretation biased. In addition, warm events, which occurred during winter, could cause snow melting and percolation (another disturbance factor). This can be solved by including a snow pack model that is able to reproduce snow pack evolution over time and to associate a specific depth to a specific period. Moreover, snow modelling has to be associated to back trajectories analysis in order to identify possible sources of impurities in the snowpack. We proposed this manuscript as a measurement report since we wanted to have a dedicated study focusing on the regional differences in loading. The layer by layer investigation of the Svalbard glaciers, using the data collected in the accumulation areas, will be the aim of the next paper where all the associate variables will be considered. However, if the referee would like to have our dataset to check some calculations, we can send it privately.

R: As the authors mentioned in the manuscript, the periods of snow accumulation are different from observation site to site. Therefore, load of chemical substances might be biased by the differences of the period of snow accumulation. Therefore, I believe that this measurement report should report both of spatial variations of loads and concentrations of chemical substances.

A: We agree with the referee that it is useful to add both loads and concentrations. In the previous version of the manuscript, we attempted to address this by calculating the correlation coefficients both for loads and for concentrations. However, as suggested by referee, we added a new table with volume-weighted mean concentrations of major ions in each snow pit (calculated as the sum of concentrations in all layers divided by the total SWE of the snow pit) in this revised version to improve clarity.

R: Moreover, I can imagine that the spatial variations might be different from in autumn, winter, and early spring. Therefore, the vertical profiles of chemical substances indicating seasonal variations are also valuable. I also have several concerns about the evaluations of the spatial variation in the results and the discussions.

A: We are agree with the referee, but the identification of the seasonal variation requires snow pack modelling for each site studied and all evaluations listed in our previous answer. The aim of the paper is to understand the regional differences in the annual snow pack and not investigate the differences for each snow layer and the variables that could affect the snowpack stratigraphy. We present the paper as a measurements report since we aim to have an initial large-scale evaluation of the main processes and then specifically address the snowpack stratigraphy. We feel that this initial analysis is a critical first step before proceeding with the detailed evaluation of each layer. In addition, we feel that it is important to make our measurements available to the larger research community.

R: Specific comments R: Title: In this article, only seasonal snow (autumn, winter, and

spring) is treated. The authors should titled in such a way that the seasonal snow is made explicit.

A: We modified the title as follows: “Measurement report: Spatial variations in seasonal snowpack ionic chemistry and water stable isotopes across Svalbard”

R: L90: Valence of Na ion is 1. Na+

A: Sorry for this terrible mistake for a chemist.

R: L92: Main subject of Goto-Azuma et al. is influenced of melt water on chemical profiles in snowpack. Winther et al. does not show chemical data. I believe that there are more appropriate references. For example, Issakson et al., 2001 showed the chemical data of ice core from Lomonosovfonna, and Matoba et al., 2002 showed chemical data of snowpack and ice core from Vestfonna.

A: Thanks for the suggestion. We modified as suggested by the referee, removing Goto Azuma and Winther and adding Issakson et al. and Matoba et al.

R: L124. This protocol was used for the project of C2S3 and was not authorized by international organizations. Therefore, please change the description to avoid misunderstandings and describe more details of the method.

A: As suggested by referee 1, the protocol is not authorized by international organizations, so we removed “standardized” from the sentence. In the manuscript, we included the description of the main points of this common protocol.

R: Major ion analyses 2.2 Major ion analyses. Please unify the items described in each analytical condition in each laboratory. Please added followings: Flow rate of IC at Hornsund and Venice. Information of the guard column in Uppsala Filtering method in Venice Authors used the terms “eluent” in Hornsund, and “mobile phase” in Uppsala and Venice. Please unify the term.

A: We unified the analytical conditions description in each lab, adding the flow rate at

Hornsund and several method details at Venice lab (gradient condition, flow rate). We used “mobile phase” in each description.

R: L158 Cation was determined in Uppsala.

A: Yes, this is the description of cation determination, as suggested by the column and mobile phase. Sorry for the mistake.

R: L174 In Barbaro et al., 2017, analytical methods of amino acid were described, but not of anion and cation. Please cite appropriate references.

A: We agree with the referee, this reference is wrong. We modified the reference to the correct Barbaro et al. 2017. (Barbaro et al. Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol. Environmental Science and Pollution Research, 2017, 24.3: 2724-2733.)

R: 2.2.4 Instrumental performance of each laboratory. I suggest that this part is described in the first chapter of 2.2.

A: We feel that introducing the instrumental analysis details and then describing the instrumental performance of each lab provides more clarity.

R: 3. Result As the authors mentioned, the periods of snow accumulation are different from observation site to site. Therefore, load of chemical substances might be biased by the differences of the period of snow accumulation. To evaluate the impacts of chemical substances on the environment of snowpack in Svalbard, the total loads of chemical substances are appropriate. On the other hand, to evaluate the transport process of chemical substances from the other regions to Svalbard, the concentrations of chemical substances are also appropriate.

A: In the submitted manuscript, we have already considered the data both as load and as concentrations (“we computed Spearman rank correlations between total ionic loads (load), as well as between volume-weighted mean ionic concentrations (conc)”). On the other hand, we agree with the referee that we have to add a new table (Table

3) with the raw data of the volume-weighted mean concentrations of each ion. We add these sentences in the manuscript: “On the other hand, to evaluate the transport processes of chemical species from the other regions to Svalbard, we evaluate the volume-weighted mean concentrations of major ions in each snow pit. These values are calculated as the total ionic load of each snow pit divided by its total SWE (snow water equivalent) (Table 3).”

R: L216 Please add the names of observation sites as “Hornsund area (HB and WB, southern Spitsbergen)”

A: Thanks for the suggestion, we added HB and WB inside the brackets.

R: L219 same zone -> accumulation zone.

A: We substituted “same” with “accumulation”.

R: L223 Figure S1 is important data and should be in the main text, and not in the supplemental materials.

A: As suggested by referee 1, we moved figure S1 (now Figure 3) into the main manuscript and we corrected all following figure numbers.

R: L216 “Hornsund area” L230 “Hornsund region”, L234 “Hornsund glaciers” Please unify them.

A: We now use always “Hornsund area” instead of “Hornsund region” but we maintained “Hornsund glaciers” because this refers to “snowpack on Hornsund glaciers”.

R: L241 Figure S2 is important data and should be in the main text, and not in the supplemental materials. The spatial variation of water stable isotopes is very important.

A: As suggested by referee 1, we moved the Figure S2 (now Figure 4) in the main manuscript and we corrected all following figure numbers.

R: L246 Please add the names of observation sites in “NW Spitsbergen (XXX, XXX).

A: As suggested by the referee, we added "(KVG, ALB and HDF)".

R: L250-253 I could not catch what the authors would state.

A: To clarify the statement, we simplified as follows: "On the other hand, AF, WB, and HB there was no statistical difference between the mean δ18O and δ2H values (Figure 4). "

R: 4. Discussion. Temporal variations of chemical substances are not subjects of this article. Therefore, the part L257-265 is not necessary for this article.

A: We included this part because we want to compare our data with previous measurements reported in the Svalbard glaciers. The state of the art is important to define if our data is comparable with previous studies (i.e., representative for more than just the 2015/16 accumulation season).

R: 4.1 Why not specify the percentage of sea-salt derived components in all chemical species, and show the prominence of sea salt as an origin?

A: In Table 3, we included the volume-weighted mean concentrations of major ions in each snow pit (calculated as the sum of concentrations in all layers divided by the total SWE of the snow pit). Here we included also nss-SO42-, nss- K+, nss- Mg2+, nss-Ca2+. The discussion about these fractions is reported in the main manuscript.

L281-288 For this discussion, nss-Mg2+ should be used rather than total Mg2+.

A: As shown in the table 3, the concentrations of nss-Mg2+ are frequently negative. Therefore, to avoid introducing extra uncertainty, we avoided performing a correlation with Ca2+ and nss-Mg2+.

L297 Generally, SOx does not originate from biomass burning. Does the authors mean the transportation of the secondary aerosols of ammonium sulfate formed by SOx from coal combustion and ammonium from biomass burning?

A: To clarify the concept, we modified the sentence as follows: "Another plausible

source of nss-SO42- deposition in Svalbard is long-range atmospheric transport of secondary aerosols containing SO42-, such as ammonium sulfate. This sulphate can be formed by SOx emitted from coal combustion throughout the winter and biomass burning in the spring (Barrie, 1986; Law and Stohl, 2007; Nawrot et al., 2016)"

R: L298-302 I could not catch what the authors would state.

A: We clarified the concept as follows: "However, we need to caution that in the southern region of Svalbard, the estimation of ss-SO42- is subject to higher uncertainty because of the higher amount of Na+ in the atmospheric deposition there."

L304-312I could not catch what the authors would state. At the ocean around Svalbard, algae bloom can occur in autumn. I am not sure that the autumn bloom can affect the snow chemistry in Svalbard. I just cite a reference (Andyna et al., 2014)

A: We refer to the algal bloom that can occur in May or late spring. In our recent publication (Spolaor, Andrea et al. "Source, timing and dynamics of ionic species mobility in the Svalbard annual snowpack." Science of The Total Environment 751 (2020): 141640.), the dynamics of ionic species are investigated and we found an increase in surface concentrations of sulphate and MSA during May. The sampling performed in April can underestimate the impact of nss-SO4 coming from biogenic sources.

R: 4.2 Chlorine depletion L349: Under the reaction of chlorine depletion, sea salt NaCl reacts with acid. Therefore, the acid should be described as HNO3 and H2SO4 instead of NO3- and SO42-.

A: We completely agree with the referee because the reactions are the following: HNO3 (aq) +NaCl (aq,s) → NaNO3 (aq,s) + HCl (g) H2SO4 (aq) +2NaCl (aq,s) →Na2SO4 (aq,s) +2 HCl (g) We modified it as suggested by the referee.

R: L351 The weight ratio of Cl/Na is 1.8. 1.174 is the mole ratio of that. In this paper, weight units are used for loads of chemical substances. In Figure 3, Cl/Na ratio is 1.80. Please change the number of Cl/Na and confirm the calculation of Cl depletion rate.

A: Figure 3 (now 5) reports the weight ratio and 1.8 is corrected as also confirmed by referee. The values of Cl depletion (%) were calculated with the formula reported in the manuscript and we used the equivalent concentration to calculate the Cl depl. Therefore, we can confirm that the values of Cl depl are correct.

R: Whitlow et al., (1992) indicated that Cl/Na in snowpack at the Summit of Greenland was higher than the ratio of seawater. According to this paper, Cl depletion occurs on aerosol particles and the Cl-depleted aerosol particles are scavenged during the transportation of air mass. Thus, Cl/Na of residue of air mass becomes higher values. On the other hand, Cl/Na in Svalbard is lower than seawater in this article. If the authors indicate the characteristics of snow in Svalbard based on the difference from Greenland, the worth of this article should be higher.

A: Thanks for the suggestion; we introduced a comparison between Cl/Na in the snowpack of Svalbard and Greenland. We introduced these sentences in section 4.2: “Withlow et al. (1992) found an opposite situation in the snowpack of Greenland, indicating Cl-/Na+ values higher than the ratio of seawater. This Cl- enrichment relative to the Cl-/Na+ ratio in sea water may reflect Cl derived from anthropogenic sources as well from gas phase chlorine transportation and deposition in central Greenland.”

R: 4.3 Br enrichment Hara et al., 2017 showed that Br was concentrated on frost flowers formed on new sea ice before the end of polar night, and consistent with this article.

A: We thank the referee for finding similarities between our results and Hara et al. 2017. The Br enrichment (or depletion) in the snowpack is not only due to physical atmospheric sea spray transport (or Br from frost flowers on sea ice) but also to the atmospheric chemical processes that can alter its signature The aim of the paper is broader than Br chemistry, which is why we chose not to go into the details of Br atmospheric processes, but their description is reported in the references cited. Bromine activation requires higher amounts of salts to sustain the “explosion” and the sea ice surface (mainly first-year sea ice) is the perfect substrate to start the so-called bromine

explosion. However, frost flowers might not be the direct source of extra bromine, since no fractions of Br compared to Na have been determined and suggested. On the other hand, frost flowers could be a source of gas phase bromine, although not the only one, since the snow over sea ice can act as a source. Hara and co-authors did their study in Antarctica where sea ice is mainly as first-year sea ice. The sea ice around Svalbard is also mainly first-year ice, but the sea ice drift occurring in the Arctic basin could replace the first-year sea ice with multi-year sea ice, making the condition different. This process is rather evident in the Fram Strait where a large amount of sea ice is expulsed from the Arctic basin.

R:4.4 L394 “*” is used for PC calculation.

A: We removed “*” and we added “Âů” to indicate the multiplication.

R: L395 d-excess is influenced by not only SST but also relative humidity and wind speed (Gat, 1996; Uemura et al.,2008)

A: We modified the sentence as follows: “Deuterium excess (d = δD-(8Âůδ18O)) is mainly influenced by the source region of the precipitating moisture and in particular by the sea surface temperature, but also relative humidity and wind speed.”

R: 4.5 L426-429 If the water vapor is long-range transported from lower latitude, isotopically heavier molecules should be removed from air mass during the transportation and delta value of 18O should be decreased. Moreover, it is not understandable that Na from sea splay is accumulated in air mass during the transportation of air mass from far south. Because, the amount of Na scavenged from the air mass is much larger than that input from sea spray on the ocean surface. I believe simply the reason for the correlation between d18O and Na concentration in the high latitude area is as below: At high latitude areas, air mass is transported from simply from low elevation site to high elevation site without any strong disturbance of atmospheric condition. In this case, isotopically heavier molecules and chemical substances from sea spray are scavenged from air mass gradually. Thus, d18O and Na concentration shows positive correlation.

A: We thank the referee for this comment. We agree with some aspects and have modified the text in the manuscript accordingly. We think that the explanation of the correlation between δ18O and Na is not straightforward and a few hypotheses should be considered. However, we do not think that a simple atmospheric distillation is the main reason, because otherwise the same correlation should be found at any elevation, assuming a similar δ18O and Na fractionation. We agree that the sodium might not be collected during air mass transport from lower latitudes and we removed this hypothesis as suggested by the referee. The text has been modified as follows: "The increase in strength and significance of the log(Naload)-δ18O correlation with altitude might be explained by different contributions of locally emitted ssNa+, relative to those of Na+ from more distant sources. Sites located at lower altitudes are proportionally more affected by local sea spray deposition, with or without snowfall. Conversely, sites at higher elevations likely receive a larger share of their ionic load from more distant sources, and by wet deposition through snowfall. At the four sites (KVG, AF, LF, and HDF) where the log(Naload)-δ18O correlation was significant, increases in δ18O in snow layers were often associated with higher Na+ concentrations. It is rather difficult to propose a precise explanation for this association. However, we would suggest that the isotopically heavier (less negative) δ18O values suggest that the co-registered Na+ enhancements were associated with precipitation of relatively warm air, probably advected from lower latitudes. The snowfall associated with a warm event is able to wet scavenge the sea spray aerosol present in the atmosphere. On the contrary, when the cold air masses (Arctic type) dominated, the snowfall events were relatively limited due to the poor air humidity causing a lower efficiency of wet scavenging. This resulted in lower δ18O and (likely) Na sodium loads, suggesting that wet deposition dominated the chemical load of the snowpack. Although this process is should occur also at lower elevation sites, the local emission and associated dry deposition are likely more important than wet deposition; more frequent melt-refreeze episodes at lower elevations would also mask the relationship proposed (as suggested by the vertical profiles of stratigraphy reported in Figure S4). Another possible explanation is that in the Arctic, air masses are transported from low to high elevation sites without any strong disturbance of the atmospheric conditions. In this case, isotopically heavier molecules and sea spray particles are gradually scavenged from the air masses. If this was the main process, we should find the correlation across all studied sites, assuming that Na+ scavenged at a similar rate as that of isotopic fractionation. Since this has not been found, we propose that the correlation at higher elevation cannot be explained by atmospheric distillation alone. The possibility that the correlation is due to different sources of air masses seems unsupported due to the absence of correlation between d-excess and sodium."

R: L532 Goto-Azuma et al., The name of the journal is "Publication of the International Association of Hydrological Sciences".

A: We modified the name of the journal as suggested by referee.

R: Figure 2 Caption. Please describe the name of observation site in the figure caption.as "HDF; Holtedahlfonna". KV should be KVG.

A: Done

Table 1 What does the "air temperature" in Table 1 indicate? Please describe time and date.

A: As suggested by the referee, we clarify the parameter in the caption as follows: "The air temperature was measured with a digital thermometer when the operators started to dig the snow pits."

References for this review. Andyna, M. et al., 2014, Geophys.Res.Lett.,41, doi 10.1002/2014GL061047. Hara et al., 2017, ACP, 17, 8577-8598.doi:10.5194/acp-17+8577-2017. Issakson et al., 2001, J. Glociol., 47, 335-345. doi:10.3189/172756501781832313 Matoba et al., 2002, J. Geophys. Res., 107, D23,4721.doi:10.1029/2002JD002205

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2020-740/acp-2020-740-AC1-supplement.pdf

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