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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: The paper presents the results of a snow chemistry survey carried out on several glaciers across Svalbard in the spring season. The authors analysed snow pit samples for their major ion loads and stable water isotope composition in order to understand the spatial distribution pattern of different chemical species in the snowpack across the archipelago. The comprehensiveness of the presented data set makes it valuable for improving our understanding of which role transport processes, deposition patterns and sea ice formation processes play for the chemical composition of the seasonal snowpack on Svalbard. Therefore, I suggest the manuscript to be published in ACP

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Discussion paper

as a measurement report. However, according to the title of the paper setting focus on both ionic chemistry and stable water isotopes of the snowpack I am missing a more detailed description of the stable water isotope survey, in the methods, results and discussion section. From the introduction it does not really become clear to me for which reason stable water isotopes are analysed in this study. What is the major aim of the stable water isotope analyses and what is the connection to the ionic composition? What do you want to explain with the help of the stable water isotopes? I also propose to give a short overview of the current knowledge about stable water isotopes in snow on Svalbard in the introduction as it has been shortly done for the chemical impurities.

A: Thanks to the referee for the comments. We improved the stable isotope description to clarify the aim of the use of these ratios in the manuscript and to describe the state-of-the-art of these measurements in the Svalbard snowpack. Please see the specific comments where we reported all modifications.

R: Furthermore, in order to understand the distribution pattern of major ions and stable water isotopes on Svalbard I think it is highly necessary to give more details on the different glacier sites, i.e. about their similarities and differences regarding size, shape, exposition to wind, distance to the sea ice edge.

A: As proposed by the referee, we included a new paragraph where we described each glacier monitored.

R: At the moment the authors provide values for ionic loads and stable water isotopes only as values summed up or averaged over the entire depth of the snowpack that has been sampled. Hence, I think that it is of high value for the manuscript if also the vertical distribution pattern of the ionic composition and of stable water isotopes is included as this can deliver additional information about seasonal differences in transport processes, moisture sources and accumulation. Therefore, I strongly recommend to add a chapter about the stratigraphic differences and similarities regarding the ionic load and the stable water isotope composition to the Results chapter of the manuscript.

When explaining the observed spatial differences in the ionic and isotopic composition of the snowpack at the different sites, I also strongly suggest to discuss the role of post-depositional processes, in particular the reallocation of snow, and thus reallocation of ions and isotopes due to wind drift in more detail. Katabatic winds blowing down glacier valleys might cause significant removal, redistribution and redeposition of snow and thus might bias the ionic and isotopic composition of the snowpack. It is necessary to consider the aspect of wind drift in particular when trying to explain unexpected distribution patterns of ions and stable water isotopes (e.g. lack of altitudinal gradient in the stable water isotope composition).

A: We thank referee 2 for this comment and it is also a point raised by referee 1. We beg to differ at this point: we think that presenting the data at layer resolution will exceed significantly the intended scope of this manuscript (there could be a whole paper written on that topic, which is in preparation). In this paper, we present and discuss the spatial and altitudinal differences in the loads of several chemical species. The evaluation of the layer composition requires extensive scientific discussion and modelling work. In snow pits, it is rather difficult to associate a specific layer with a specific period and this makes the interpretation biased. This can be solved by including snow pack modelling to reproduce temporally the snow pack evolution and so to link specific depths to specific periods. To identify possible sources of impurities in the snowpack, such studies should be complemented by air mass back trajectory analysis. In addition, warm events occurring during winter could cause snow melting and percolation (another disturbance factor). A detailed insight into all these processes was not the aim of this manuscript, on the contrary, we mainly focused on characterising and identifying regional differences of chemical species across Svalbard. For this reason, we omit the description of the vertical snowpack profiles for each site and we focus the discussion only on the total load. For fair assessment of our work (e.g., to check the calculations), we are happy to make the layer-resolution dataset available for the reviewer, but we do not intend to publish it in this Measurement report.

Specific comments: R: Title: The title should also indicate the seasonal aspect of the study.

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

Abstract: L46 Please write δD instead of $\delta 2H$ throughout the manuscript as this is the most common notation.

A: We agree with the reviewer that different notations can be used and that most journals accepted both versions. δD is historical and a new "Unit" was proposed in the SI system about 10 years ago. This unit has not been used widely, but as compromise today most people use $\delta 2H$ and not δD. (δD is not included in the SI-system). We based the use of $\delta 2H$ on the following references. References Dunn, Philip & Carter, J.F.. (2018). Good Practice Guide for Isotope Ratio Mass Spectrometry Second Edition 2018. Pag 8 Brand, Willi A., et al. "Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report)." Pure and Applied Chemistry 86.3 (2014): 425-467. Meier-Augenstein, Wolfram, and Arndt Schimmelmann. "A guide for proper utilisation of stable isotope reference materials." Isotopes in environmental and health studies 55.2 (2019): 113-128.

1. Introduction: R: L81-82 It is unclear where the last part of the sentence ("...and has also experienced...") refers to – the west or the east of the archipelago. Please rephrase.

A: We modified the sentence as follows: "the west exhibits higher temperatures and precipitation, while the east is less humid and cooler, and has also experienced a stronger warming trend since 1957."

R: L 84-98 Please add some information about the state-of-the art of the spatial distribution of stable water isotopes in the snowpack on Svalbard

A: We added a small paragraph in the introduction to define the state-of the art of stable

isotopes in Svalbard.

R: L 100-110 Please state clearly what stable water isotopes are used for in this study, i.e.what is the objective connected with the analysis of stable water isotopes.

A: To clarify the aim of stable water isotope determination we added this sentence: "Stable isotope ratios were used as supporting data to define the accumulation seasonality in snowpack, and to identify the moisture sources that feed snowfall, thereby providing clues to the predominant air transport pathways to the snow pit sites (Gat et al., 2001)."

2. Methods: L 118 Please give more details on the different glacier sites. How different are they regarding their size and shape? How are they oriented, i.e. what is there flow direction (N-S, W-E)? Are there differences in their exposition to wind (e.g. U-shaped valleys vs. plateaus)?

As suggested by referee, we added a new part with the description of each glacier.

L122 Where does "these zones" refer to? Accumulation and ablation zones or the ELA? Please be precise here.

A: As suggested by referee, we added "(accumulation, ablation, and ELA)".

R: L128-129 Why do you use different sampling resolutions at the different sites? Treating all sites in the same way would increase the comparability of the data that you derive. Please explain why you use this sampling strategy.

A: In this work, we used the protocol published by Gallet al al. (2018). The authors clearly reported the advantage of sampling per discrete layers. This type of sampling allows to link a snow layer (and its properties) to a specific climate event (i.e. precipitation or surface melt). The investigation of ionic composition of snow helps to identify the atmospheric sources of impurities deposited in the snowpack during a specific snow accumulation period. Moreover, sampling by discrete layer makes it possible to correlate intervals of snow accumulation between separate snow pits at different altitudes,

as reported in this paper when we compared the three different areas in the same glacier (ablation, ELA and accumulation). For the purpose of total load calculations, this procedure is also better because it treats as entities layers which are relatively homogeneous, allowing a more appropriate inclusion of ice layers into both density and chemistry measurements. Contrastingly, the sampling by fixed depth increments is a more simple and easy procedure to use by multiple teams because it does not require a description of the snowpack stratigraphy by an expert operator. To improve the manuscript we added these sentences: "This type of sampling facilitates linking a snow layer (and its properties) to a specific weather event (i.e., precipitation or surface melt). Moreover, sampling by discrete layers makes it possible to correlate the intervals of snow accumulation between separate snow pits at different altitudes, as reported in this paper when we compared the three different areas in the same glacier (ablation, ELA and accumulation). It is also more accurate for chemical load calculations where ice layers occur in snow pits."

R: L 152 Delete "as recommended for this device and column" as this information is un-necessary.

A: As suggested by referee, we removed this part of sentence.

R: L198-202. The description of the stable water analysis is very short. Please give more details here: How many injections did you use per sample? How was the raw data corrected (e.g. for memory effects, drift)? Which standards did you use?

A: We improved the description of stable water isotope analysis as follows: "The determination of stable isotope ratios of O and H was performed at Tallinn University of Technology (Estonia). The isotopic ratios were determined by laser spectroscopy, using a Picarro model L2120-i water isotope analyzer (Picarro Inc., Sunnyvale, USA), which allows for the simultaneous determinations of 18O/16O and 2H/1H in H2O with a high-precision AO211 vaporizer. Results are reported in the standard delta notation as δ18O and δ2H relative to Vienna Standard Mean Ocean Water (VSMOW). Re-

producibility was ±0.1‰ for δ18O and ±1‰ for δ2H, respectively. 7 injections were carried out for each sample, but only the last 4 injections (4 to 7) were used for calculations to minimize the memory effect. Laboratory standards TLN-A2 (-10.15; -77.5) and TLN-B2 (-21.95; -162.5) were regularly calibrated against international V-SMOW, GNIP and V-SLAP standards. Standards (TLN-A2, TLN-B, and TLN-D4) were measured at the beginning, in the middle, and at the end of each set of measurements (54 bottles). Additionally, every 7 samples, the laboratory standard TLN-D4 (-17.5; -133.0) was measured and used for drift correction if needed."

R: 3. Results: It is worth to include a chapter about the vertical distribution of major ions and stable water isotopes in the snowpack, i.e. to add a chapter about the stratigraphy and the spatial differences (or similarities) between the different glacier sites.

A: Please check the answer in the general comments. We think this would need more than a chapter – rather a separate article.

R: L 241 How did you calculate the SWE-weighted mean? Please add this information.

A: As suggested by referee, we clarified this calculation: "The SWE-weighted mean δ18O and δ2H are calculated using the formula SWE-δ = $\sum$(δi x SWEi)/SWEt where δi areis the con the δ values of each layer, SWEi are SWE of each layer and SWEt is the SWE of the entire snow pit."

R: L249-251 Do you have any explanation for this unusual pattern? Due to the altitudinal effect one would expect the stable water isotope composition to become lighter with increasing height as you did observe on KGV, ALB, HDF and LF. What about reallocation of snow by wind drift? Are there differences in the exposition of the different glacier sites to wind drift? Is there any influence of the glacier size and shape on the snow accumulation pattern and thus potentially also on the distribution of the stable water isotope composition in the snow? What about post-depositional effects that might alter the isotopic composition of the snowpack, such as diffusion and sublimation? Please add some possible explanations to the discussion chapter 4.4.

A: The post- depositional processes could influence the water stable isotope signal, but there is still lack of knowledge regarding the effect of post-depositional processes on the preserved signal. For example, post-depositional processes could equilibrate the snow water stable isotope value with the average value characterising the atmosphere above the site of sampling. Defining the role of the post-depositional processes is rather difficult and giving an estimation at this point would be speculative. Certainly, wind redistribution could have an effect as well but the snow redistribution might be confined to the area of snow deposition (within < 1km). Generally the occurrence of strong wind produces the so called wind crust, an extremely hard snow layer difficult for the wind to lift. All the snow pits have been collected from the glacier central line in order to minimise the side accumulation effect due to orography.

4. Discussion: R: L 259 What do you mean by "unpublished data"? Please specify.

A: As suggested by referee we clarified this aspect: ". In table 4, we report also unpublished data of samples collected in 2009-2011 by C. Vega, obtained using the same methods reported in section 2.2."

R: L260 Finish the sentence after "firn cores" and start a new sentence "Our study...".

A: As suggested by referee, we split the sentence.

R: L 286 The sentence is incomplete. Please check

A: Sorry for the mistake. We completed the sentence as follows: "which are abundant in Svalbard (Dallmann, 1999)."

L 315-319 I could not catch what you want to say here. Please rephrase and make two sentences.

A: We clarified the sentence as suggested by referee.

R: L 336-338 What do you think might be the reason for this pattern? What about long-distance transport of pollutants to the site? Please discuss.

A: The explanation of this pattern was reported in the following sentences: "The highest correlation coefficient for NO3-, both in terms of concentrations and loads, was found with nss-Ca2+. This would support both the formation of calcium nitrate in the atmosphere (Gibson et al., 2006) or post-depositional processes removing the NO3- from layers poor in Ca2+, since calcium has been hypothesised to stabilise the nitrate in snowpack against post-depositional losses (Kekonen et al., 2017)."

L395 The d excess is also influenced by the relative humidity in the moisture source region.

A: As suggested by both referees, we specified this aspect as follows: "Deuterium excess (d = δ2H-(8·δ18O)) 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 (Gat, 1996; Uemura et al., 2008). In addition, d is also influenced by the temperature gradient between the moisture source and precipitation area (Johnsen et al., 1989)."

L 399-401 Please explain what the Kruskal-Wallis test is and what it is used for in general (statistically). Just from the values in Table 2, I cannot see a significant difference between the d excess values at AF and the other sites, e.g. a d excess of almost 17‰ also occurs at HDF3, values > 14‰ also occur at ALB1 and ALB2.

A: To clarify this concept, we modified the sentence as follows: "more detailed analysis of d by latitude showed that only significantly different values were obtained in snow pits sampledonly beyond 79.2 °N, i.e., in Austfonna snow pits. This is confirmed by (the Kruskal-Wallis test, , i.e. rank-based ANOVA, calculated with two groups of d values divided by the latitude threshold 79.2°N; z = 4.23, p < 0.04; in fact, drawing the latitude threshold anywhere between 78.7 and 79.7 °N resulted in a statistically significant difference with p < 0.05)."

L 414. Actually, the d excess is the parameter that provides information about moisture source variations. δ18O is rather related to the condensation temperature at the

precipitation site. I suggest to also calculate the relation between log-transformed Na+ and the d excess and to compare the results with the relation between log-transformed Na+ and δ18O.

A: Thanks to referee for this comment, similar to the observation of referee 1. We agree that the increased sodium concentration might not be related to the longer atmospheric pathway above the ocean surface but might be also linked with the wet scavenging occurring during a snowfall event. The correlation determined is not due to the source but instead the occurrence of a snowfall able to clean up the atmosphere and normally associated to relatively warmer and wetter air masses as compared to the Arctic type. This hypothesis is also supported by the lack of correlation between d-excess and sodium in our dataset. The d-excess in this case is not useful since, as the referee states, it is an indicator of air mass sources. We modified the main manuscript as follows to better explain the correlation between log(Naload)-δ18O: "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: L 430-433 What about reallocation of snow by wind drift? Depending on the exposition of the site it can significantly alter the ionic and isotopic composition of the snow after deposition.

A: As reported in the previous answer, wind drift is a very important topic that this paper cannot appropriately solve. We dug the snow pits along the central line in order to minimize the orography interferences. However, the effect of wind should be limited due to the formation of wind crust. We admit that the reallocation of chemical species in the snowpack is a very interesting topic but we would need another type of experiment to evaluate it. Here, the aim is to define the spatial distribution of chemical loads.

R: Figure 1: Please add all glacier site abbreviations to the figure captions.

A: We added this sentence: "Abbreviation: KVG = Kongsvegen, HDF = Holtedahlfonna, AF= Austfonna, ALB = Austre Lovénbreen, LF = Lomonosovfonna, HB = Hansbreen, WB = Werenskiöldbreen."

Technical corrections: I suggest to use present tense throughout the manuscript whenever you are talking about results, in particular in the following paragraphs: L48-55, L216-253, L 281-288,L 290-302.I also strongly recommend to make shorter sentences in order to increase the readability of the text, in particular in the following paragraphs: L58-59, L74-78, L105-108.

C11

A: We modified the entire manuscript as suggested by referee. R: L106 Add comma after the bracket.

A: Done

R: L124 Delete one dot behind "i.e." in the bracket.

A: We removed the comma after i.e.

R: L154 Delete the commas enclosing "as well as DPA".

A: Done

R: L155 Add "the" before "solid phase".

A: We added "the"

R: L174 Delete the bracket before "Barbaro et al." and enclose 2017 by brackets.

A: We corrected the reference.

R: L177 Use plural for "calibration".

A: We substituted with plural.

R: L 178 Consider to use "delivered" instead of "gave".

A: We used "delivered" instead of "gave".

R: L183 and L184 Add "all" before "cases".

A: We added "all" before "cases"

R: L186 Add "the" before "bulk ionic load".

A: We added "the".

L214 Delete the comma after ELA.

A: We removed it.

L216 Replace "snow pits samples" by "snow-pit samples".

A: I think that "snow pit" it is correct.

R: L 258-259 Delete the bracket before "Virkkunen et al." and enclose 2007 by brackets. The same for "Vega et al." (delete the bracket before and enclose the year in brackets).

A: We modified as suggested by referee.

R: L 263 Delete the bracket before "Spolaor et al." and enclose 2013 by brackets.

A: Done

R: L 278 Add "the" before "snowpack".

A: We added it

L 284 Too many brackets re-write: (0.32; Millero etal., 2008; Figure 3).

A: We modified as suggested by referee.

R: L292 Write Cl-/SO42- instead of Cl-:SO42-. Add "on" before "those".

A: Done

R: L 300-301 Delete "which is a derived variable" as this has been explained before.

A: We removed the sentence inside the commas.

R: L 312 Add "an" before "underrepresentation".

A: We added "an"

R:L 359 Add a dot after the bracket and delete "and".

A: As suggested by referee we inserted a dot and we added an "and".

R: L 368 Delete the comma after "always".

A: We removed bot commas.

C13

R: L369 Delete the bracket before "Jacobi et al." and enclose the year by brackets.

A: Done

R:L 379 Delete the space after "this".

A: Done

R: L 400 "was" needs to be shifted behind "d".

A: We removed "d" because it is a repetition of the previous "a more detailed analysis of d by latitude".

R: L 411 Delete the comma after "higher".

A: Done

R: L 417 Replace "glaciers sites" by "glacier sites".

A: We removed "s"

R: L 428 Replace "suggests" by "suggest".

A: We removed "s"

Figure 2: Replace "glaciers zone" by "glacier zones".

A: Done

Figure 3: L 705 Delete "the" before "spring".

A: We removed "the" from now figure 5.

Figure 5: L 726 Add "the" before "oxygen".

A: We added "the" from now figure 7.

R: Table 1: Replace "Universit! de Franche-Comté" by "Université de Franche-Comté".

A: This is correct but probably something occurred during the pdf conversion.

Table 2: Replace "compare to sea water" by "compared to sea water". Please also add the unit forδ18O, δD and d excess in the table captions.

A: We modified "compared to seawater" and we added the unit for the stable isotopes.

Table 4: Add a comma after Millero et al.

A: We added comma after "Millero et al."

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2020-740/acp-2020-740-AC2-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-740, 2020.