Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-742-RC2, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical composition and source attribution of submicron aerosol particles in the summertime Arctic lower troposphere" *by* Franziska Köllner et al.

Anonymous Referee #2

Received and published: 22 September 2020

Kollner et al present summertime aircraft-based online aerosol chemical composition data from two mass spectrometers, providing both single-particle and bulk composition information, which is quite unique. These novel data were collected as part of the Canadian NETCARE campaign and significantly contribute to understanding of Arctic summertime aerosol composition, knowledge of which is observationally limited, especially when considering non-ground-based measurements. This is an important dataset to publish. Overall, the paper is well-done and contributes significantly to the field. The vertical profiles of aerosol composition and source region analyses using backward air mass trajectories are a good analysis approach to correlate composition with air mass source regions. It is excellent that the authors scaled the ALABAMA

data to number concentrations and conducted uncertainty analysis. The supplementary material is comprehensive. However, I have one major data analysis concern, as described below, about the significant fraction of unexamined single-particle data, the omission of which potentially impacts the presentation and interpretation of the results. In addition, as described below, the authors' definition of "Arctic" as north of 73.5 deg is inconsistent with its geographic definition and norms of other studies, and impacts the source region attribution and discussion. Otherwise, the majority of my other comments are minor.

My major data analysis concern regards the approach in the classification of the ALABAMA single-particle mass spectra. As stated on lines 140-141, "the ion marker method classified particles based on the presence of pre-selected species that are of interest." This means that the authors have chosen what chemical species to focus on, which is not necessarily problematic; however, only 54% of the single-particle mass spectra were classified. This means, as shown in Figure 6 and stated in the Figure S9 caption and on line 320, that 46% of the single-particle mass spectra are not included in the discussed data/results. Being nearly half of the ALABAMA data and the fact that this paper is meant to be an overview/summary of the results during NETCARE, I am concerned that the authors may inadvertently be biasing their results by not classifying the remaining data, and I do not consider 46% to be an acceptable fraction of unclassified/real spectra. Figure S9 shows that at least the majority of these mass spectra are real, and therefore, they need to be classified and discussed. Figure 6 shows that this requires further ion marker searches to classify the particles, and a good starting point for this is the examination of the mass spectra shown in Figure S9. In their previous paper (Kollner et al 2017, ACP), which focused on trimethylamine-containing particles, they included an additional particle type called "K-containing" (potassium-containing). Figure S9 shows the mean mass spectrum of the "Others" (non-classified) particles, and this shows a dominant K+ peak, carbonaceous ions, and sulfate. Figure S9 is also nearly identical to the mean K-containing mass spectra in Figure 4e of Kollner et al (2017, ACP). Since this particle type is consistent with biomass burning (the mass

spectrum of which is discussed on lines 441-444), it seems even more important to include a K-containing, or similar, particle type to classify more of the remaining data. Given the similarity of Figure S9 to biomass burning, it is necessary for these data to be included in the evaluation of the vegetation fire influence portion of the manuscript in particular. How does the PF.N>320 vs vegetation fire PES fraction compare for when all K-containing particles are included, or how does it compare currently for this "Others" category as a starting point? Conducting a K+ search on the remaining mass spectra will also be informative to then examine the mean mass spectra of the still unclassified particles, which can be further classified to potentially unearth another particle type that may provide greater insights. It is possible that by including more of the available data that some of the presented trends may change, or new trends may emerge, and without including more of the available data, I am concerned about the results being biased by the chosen ion markers.

Section 2.5.2 & Figure 3: Why does the category of "Arctic open water" not include the full Arctic Ocean, including the Beaufort and Chukchi Seas? Figure S36 shows some surface influence from this region, so inclusion of only open water north of 73.5 deg means that additional Arctic open water is instead classified as "Alaska" and missed in the "Arctic open water" source sector analysis. The authors could sub-categorize the High Arctic, but the full Arctic Ocean should be considered as "Arctic" for consistency with its geographic definition and for comparison to other work. This is also true with respect to the definition of 73.5 deg north as "Arctic", when the Arctic Circle is at 66 deg 34' N. Given little population north of the Arctic Circle, it would seem more appropriate to either sub-divide the Arctic into two categories, or include 66-73 N in the Arctic category. The categories of Alaska, northern Canada, Europe, Greenland & the Atlantic, and Siberia extend much, much further north, and therefore, air mass influence still in the "Arctic" (i.e. >66 deg N) would be discussed as being from a further south influence with the categories shown. The full geographic domain of the Arctic should be considered in the source region categorization. This is important since Lines 297-298 state that "The cumulative contribution of all regions outside the Arctic dominated air mass

history within the lower troposphere, making up to 97% of the PES", but this is likely partially due to the definition of "Arctic" in this work. For example, if the Beaufort and Chukchi Seas were included in the "Arctic open water" in Figure 8, would the trend be even stronger?

Figure 4b: What do the areas "not categorized in the selected geographic regions" correspond to? At >3 km, this corresponds to >20% of the data, and yet Figure 2 shows that all of the Northern Hemisphere north of 25 deg, except northern Africa, should be included in the source sector categorization. I'm also concerned about the use of 15 days of backward trajectories in terms of the associated spatial uncertainties in these trajectories, which I couldn't find to be addressed. Have the authors done analysis to validate or assess the uncertainty in the trajectories?

Additional comments: Intro, Lines 58-61: This sentence states that the references provided are "recent studies demonstrat[ing] gas flaring and shipping", but several of these studies examined oil and gas extraction activities and not specifically flaring. Further, the cited Winiger et al 2017 (PNAS) study shows flaring to be a minor BC source, and the more recent Winiger et al 2019 (Sci Adv, not currently cited in this work) also showed that the BC isotopes were not consistent with flaring. Therefore, this sentence needs to be revised to more accurately reflect the results in the manuscripts cited.

Intro, Lines 64-66: A missing and important summertime Arctic airborne study is ARCTAS-B campaign, which included flights over the Canadian Arctic during July 2008. See Matsui et al (2011a&b, JGR), which also included SP2 BC data and air mass source analysis, making it well-suited to also be considered by the authors for comparisons to the results herein.

Intro, Lines 66-68: Please consider revising this sentence. The ground-based studies can report the influence of long-range transport on the BL composition, but the strength of this work is the examination of the varying influence across the vertical column.

Methods, Lines 156-157: This needs to be rephrased because scaling to number concentrations allows quantitation but it does not “allow for assigning particle types to different sources” as stated here, as chemical composition and air mass trajectory analysis, not the concentrations themselves, are used to assign sources.

Figure 4 caption: Please add the dates of the Arctic and southern air mass periods in the caption for clarify and also refer the reader in the caption to Figure S1 for flight maps for context.

Figure 5: Please clarify whether an air mass can correspond to more than one source sector, as this seems quite possible. Please also clarify what is meant by: “The PES above vegetation fires refers to the 1-5 km vertical range.” Are air masses than pass within the BL above a fire included? This is confusing as worded.

Lines 278-279: Based on Figure 4a, it appears that Siberia should be the largest contributor at >3 km, but that isn’t mentioned here.

Lines 297-298: Figure 4b shows 30% Arctic in the BL, which seems to contradict the 97% outside of the Arctic quoted in this sentence.

Lines 303-304: It is stated that “the contribution of air masses that had resided above Arctic open water was significantly lower during the southern air mass period (Fig. 5b), compared to the Arctic air mass period.” However, it looks pretty similar at <200 m in Fig 5b.

Line 324: Note that the mass spectra show oxalate, malonate, and succinate, rather than oxalic acid, malonic acid, and succinic acid (i.e. paired cation is not definitively known through the mass spectra – or at least it isn’t discussed). Please use the appropriate wording throughout.

Line 325: Clarify here and elsewhere that you are referring to number percentages, since mass fractions are more commonly reported in the literature. Also, clarify whether 86% here refers to oxalate being present in 86% of the DCA-containing particles, as

this is not clear as stated here, and please clarify similar wording throughout.

Line 328 & Fig S8: To aid in the interpretation of this sentence, please label chloride and nitrate in this figure.

Figure 8: This figure and other similar figures show really nice analysis!

Lines 350-351: This sentence refers to air residence time but I don’t see time in Figure 8, so I can’t see how to evaluate this statement.

Lines 377: This statement is strange because the previous ground-based studies weren’t sampling the FT, so this seems to be an unnecessary statement. It can either be removed, or the authors can simply refer to the ground-based data as being less influenced by long-range transport, whereas this work sampled both the BL and FT, which is a strength.

Line 427: This reference seems to be missing from the reference list.

SI Section 1. Definite hit rate for the non-single-particle mass spec reader.

Fig S8: Please clarify whether this statement means that 60%, by number of the sea spray aerosol particles containing at least one DCA, as the statement is confusing as written.

Figures S11 and S14: Add missing a and b labels to figure to agree with caption.

Figure S18: This seems to show that DCA-containing particles were not observed for the southern air masses. Is that correct?

SI Equation 5 (page 24): I believe there is a typo here, as the definition of uncertainty for binomial statistics should be: sigma = sqrt((PF(1-PF))/N). If this typo impacts the data uncertainties shown, then please fix throughout.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-742, 2020.