Reviewer 2

Schneider et al. present a detailed assessment of carbonaceous aerosol in Siberia, commenting on topics such molecular-level characterization, plume aging, trajectory analysis, and optical properties. Their multimodal approach used allows for a broad range of molecular coverage, and the findings are well-supported by visuals throughout. While the investigation is well-written overall, I have several concerns detailed below that I believe should be addressed prior to publication.

Comments:

Title: I don't believe that the title of the paper is suitable, as 'comprehensive' and 'unprecedented' are both somewhat misleading. To this point, 'comprehensive' implies a complete characterization of the carbonaceous aerosol. And while the data interpretation herein is indeed detailed, it is largely limited to MS1 observations (i.e., lack of isomeric and structural resolution), and therefore should not be referred to as comprehensive. Use of the word 'unprecedented' is described in a later comment.

Response: We thank the reviewer for the explanation and removed "comprehensive" from the title. However, the plume transportation event was indeed unprecedented, which we explain more in detail below.

Page 2 Lines 19 – 20: the authors cite a lack of studies on Siberia as motivation and provide a single 2007 reference. However, it appears that there has been more recent work characterizing similar types of samples, and should be cited accordingly (e.g., https://acp.copernicus.org/articles/23/2747/2023/; https://www.sciencedirect.com/science/article/pii/S1352231021000595; https://www.mdpi.com/2072-4292/14/19/4980)

Response: We thank the reviewer for this comment and try to clarify our intention about the title. Indeed, long-range transport of wildfire aerosol from Siberia does occur and is not an unprecedented event. However, we were unable to find such an event with a) comparable concentrations in respect to the distance of the source and b) apparent transport into the Arctic circle. In May et al. and Johnson et al., Siberian wildfire aerosol was transported over Bering Sea to the US around the polar circle, but did not enter the Arctic. (May et al., 2023; Johnson et al., 2021) We agree that such events appear more frequently. The study by Tomshin & Solovyev (2022) covers the same event as in our study and emphasize the extreme fire season of 2021 associated with high aerosol optical depths and transport toward the North Pole. (Tomshin and Solovyev, 2022)

In the second paragraph of the introduction, we cite two studies on transportation of biomass burning aerosol to the Arctic (Yue 2022; Cali Quaglia 2022) and two about long-range transport of wildfire aerosol specifically from Siberia (Ikeda & Tanimoto 2015; Semoutnikova 2018). The lines 19-20 the referee is referring to put the number of studies from Siberia in relation to other wildfire areas (Flannigan 2009). Furthermore, weather phenomena of Siberia leading to large-scale fires are addressed on page 3 line 17-23 with three more references (Lavoué 2000; Tomshin & Solovyev 2018; Narita 2021). Therefore, we are convinced that we covered wildfires of Siberia to an appropriate extent.

Page 2 Lines 33 – 37: Some more precise langue should be used here.

Response: We modified the sentence to:
"*Moreover, heterogeneous reactions between atmospheric oxidants and particle constituents may increase the molecular complexity of primary aerosols in the atmosphere, which is associated with higher functionalization, increase in heteroatom content (O, N, S) and oligomer formation. Additionally, reaction*

between individual constituents of the particle phase complete the ongoing complex multiphase chemistry (Schneider et al., 2022; Pardo et al., 2022; Lin et al., 2015; Chacon-Madrid and Donahue, 2011)."

Page 3 Line 5: Instead of using the word 'different', please briefly describe what exactly is different to better contextualize this statement for the reader.

Response: We changed the statement to *"For example, OH radicals, the main oxidant under photochemical conditions, may be already consumed at the periphery of the plume, so enhanced photobleaching was observed at the plume edges relative to the core (Lee et al., 2020), along with faster photochemistry (Palm et al., 2021)."*

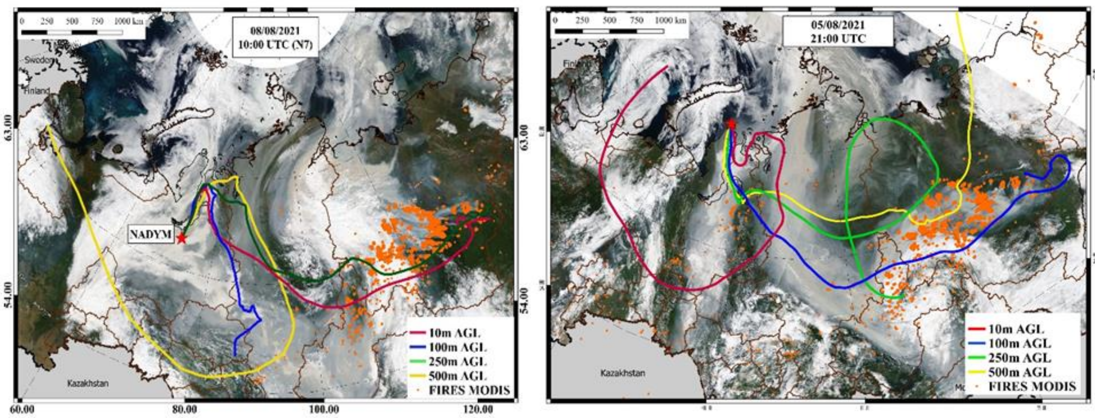
Page 3 Line 34: How high off the ground was sampling conducted? Were there any measures taken to minimize potential contribution from dust and/or ground soil particles?

Response: Filter samples were taken 4 m above sea level, so directly at the ground. Although we cannot rule out the collection of dust and soil particles, their contribution is likely very limited for the PM concentrations illustrated below.

Smoke enveloping the cities Nadym (left, https://nur24.ru/news/ecologia/smog-ot-pozharov-v-yakutii-polnostyu-okutal-yamal-foto-video) and Noyabrsk (right, https://nur24.ru/news/ecologia/smog-ot-pozharov-v-yakutii-polnostyu-okutal-yamal-foto-video) located in Yamal-Nenzen Autonomous Okrug (YNAO) in the morning of 6th August 2021

Page 4 Line 11: Expanding on the previous comment, it is imperative that the authors conduct HYSPLIT back trajectories ending with an altitude that correspond to the sample collection height. While it is great to understand the evolution of the plume at an altitude of 500m AGL, it becomes challenging to link these observations with samples that were (presumably) collected at ground level. As such, additional trajectories need to be simulated to better represent the actual sample that was collected (e.g., 10m AGL), especially since many of the authors conclusions/interpretations rely on the description of long-range transport.

Response: We thank the reviewer for addressing this issue. We studied the long-range transportation by the BWT calculations at 500 m AGL because this altitude is commonly used in the literature and regarded as the most representative. We agree that a study for the wider range including the ground level should be done additionally. In Supplementary Material (containing the figures below), the HYSPLIT calculations are presented for both Nadym (08/08/2021) and Bely Island (05/08/2021) at the range of altitudes of 10 m, 100 m, 250 m and 500 m. One can see that air mass transportation at any altitude including 10 m took place through the smoke plume covered the large territory of Western Siberia, BWT arrived to the station site from the same direction. Therefore, we show that calculations conducted for 500 m can be representative for the data presentation in this paper.



Page 6 Line 4: HYSPLIT typo

Response: The spelling is corrected to “HYSPLIT”.

Page 6 Line 6: The use of language such as ‘unprecedented’ should not be done lightly. If such a qualifier is to be used, then the authors should provide some context for why this plume is indeed unprecedented. My overall recommendation would be to soften this though, as there are plenty of other examples of extreme smoke events worldwide (e.g., 2023 Canadian wildfires that blanketed significant portions of USA and Canada in smoke).

Response: We agree with the author that several extreme wildfires and smoke transportation, but we would like to emphasize the individual fire events connected to transportation into the Arctic ecosystem. As described by Tomshin & Solovyev (2022), summer 2021 had an extreme fire season in Yakutia, being the worst for four decades, especially from 24th July to 12th August 2021, caused by high air temperature and low precipitation along with a high-pressure system. (Tomshin and Solovyev, 2022) We were unable to find a comparable event that caused TC concentrations up to 150 µg/m^{-3} 2000km distant from the BB source.

Ambient PM is continuously monitored at the Arctic Station on Bely Island, reporting weekly averages of organic aerosol <1µg/m^{-3} and BC of approximately 50 ng/m^{-3}. Our study shows more than one order of magnitude higher concentrations of OC and EC for this intense fire season, which is also 10 times the typical variation between June and September of BC at Bely Island. (Popovicheva et al., 2023) In fact, for the region of the sampling site, this event was unprecedented.

Such efficient transportation of wildfire emissions to the Arctic is linked to a rather young phenomenon called circum-Arctic wave, which is an anticyclonic anomaly. (Yasunari et al., 2021) We expect that similar events will happen in the future again, but regarding our experience at Bely Island measurement station, it is justified to call it unprecedented.

Page 6 Line 14-17: Instead of using qualitative words such as 'almost' and phrases like 'clean artic air', I recommend that the authors improve the precision in this observation my using an actual metric, such as PM2.5, to support these statements more concretely.

Response: We agree with the reviewer's suggestion and modified page 6 line 14 to

"When samples N07 and N08 were collected, OMPS aerosol index in Nadym had declined from >5 to < 0.625."

and page 6 line 17 to

"They brought clean Arctic air with an OMPS aerosol index below 0.625 from White, Barents and Kara Seas. The clean Arctic background for BC was previously determined from the 20th percentile of a 1.5 years continuous monitoring, which accounted for 10 ng m^{-3}. Background pollutant concentrations in Arctic stations are generally very low without any detectable influence from local or regional sources (Eleftheriadis et al., 2004; Popovicheva et al., 2019). Conversely, episodes of pollution were defined by the 80 percentile, accounting for 90 ng m^{-3} (Popovicheva et al., 2022)."

Page 6 line 30 – 35: this language is much more clear, but a somewhat repetitive version nonetheless of what was stated on Page 6 lines 14 – 17. I recommend merging this information for a more concise story.

Response: We intentionally created these two sections, in order to first outline the meteorological situation based on satellite data including BWT analysis and OMPS index, and secondly add results from chemical analysis.

Page 7 Line 18: The authors use sample identifies in the text (e.g., NO1), but dates in the figures. Please pick a consistent way to refer to sample to ensure easier comparison/interpretation between text and figures.

Response: We agree with the reviewer that there needs to be a consistent identifier for each sample. As in some cases, several samples were collected on the same day, only referring to a sample by its date is not sufficient.

Page 7 Line 20: Where is this data? If it is going to be presented and discussed, it needs to at least be shown in the SI.

Response: We thank the reviewer for this suggestion and added a figure to the SI. Furthermore, the typo of the correlation coefficient was changed from 0.69 to 0.59.

Page 8 Line 6 – 9: Now I have better context for the term 'unprecedented.' I would still recommend against its use overall though for reasons highlighted before. Again, an increase in concentrations by factors of ~10 is high, but likely not unprecedented given other worldwide wildfire aerosol observations.

Response: We agree with the reviewer that 10 times higher concentrations of particulate matter is not unprecedented compared to other wildfires in global context. However, as emphasized in a previous response, meteorological conditions were exceptionally favorable for generating such high concentrations in the Arctic, which was indeed unprecedented to the best of our knowledge.

Figure 3: A few of these mass spectra, particularly those for CHNO and CHO detected by APPI, CHNO detected by ESI- and CHO detected by ESI+ look as if they might be contaminated in the ~m/z 500 – 800 range. Are these major peaks that otherwise don't fit with the gaussian-like distribution separated by 44 Da? If so, there might be a significant PEG contamination issue. If yes, this is particularly concerning as PEG does not contain nitrogen – the authors peak assignments should be carefully inspected again. If these 'outliers' are instead fatty acids (high H/C, low O/C), the authors should consider manually removing them (while still describing it in the SI) as there is a strong likelihood that these are contaminant related, and not due to the sample. Further general info may be found here: https://beta-static.fishersci.ca/content/dam/fishersci/en_US/documents/programs/scientific/brochures-and-catalogs/posters/fisher-chemical-poster.pdf . This issue is perhaps further compounded/realized in Figure S5, most notbly in the top center and top right panels. Biomass burning samples are generally expected to exist as a bly in the top center and top right panels. Biomass burning samples are generally expected to exist as a continuum of species (e.g., https://pubs.acs.org/doi/full/10.1021/acsearthspacechem.1c00141), and therefore, the large 'gaps' in data here suggest that further data critiquing/cleaning is needed to ensure that all shown peaks are truly representative of the sample.

Response: We agree with the reviewer that some mass spectra from APPI, and ESI+/- show peaks that do not fit to the main Gaussian-like distribution. All mass spectra shown in the paper are blank corrected, with a field blank filter sample that was treated in the same way as the other filter samples. For blank correction, the peaks detected in the mass spectrum of the field blank were removed from the mass spectra of the samples. This is also the reason for the mentioned "gaps" in the DBE versus carbon number plots of some CHO compound classes in Figure S5, as these peaks were removed during blank correction due to their occurrence in the blank mass spectrum. We have added a more detailed description of the blank correction process to the SI.

We agree with the reviewer that especially in APPI compounds similar to typical contaminants in atmospheric pressure ionization are visible, however, as these compounds are not common in all samples and are not found in the blank spectrum, these compounds are a unique feature of the sample and it was decided against artificially removing single peaks from the data. Also, the discussion of the chemical composition is focused on relative numbers and not relative intensity of compounds, the error that may be induced by including possible contamination signals is expected to be negligible.

Figure 3-4: The authors show prominent entries for CHNOS peaks in Fig 4, but they are not shown in Figure 3. If the authors observed CHNOS, then a Figure 3-like representation of them should at least be added to the SI.

Response: We believe the reviewer is referring to Figures 4 and 5. As the number of CHNOS compounds is very low compared to the other displayed compound classes in Figure 4, except for ESI-, it is not well possible to display the CHNOS compound class together with the other classes in the Figure. We have added a mass spectrum of the CHNOS compounds in ESI- to the SI (Fig. S10).

Page 8 Line 35: while I understand that terms like 'lipid region' have been used historically to evaluate VK diagrams, it does not feel appropriate given the nature of the sample (i.e., it is not relevant to the sample or research questions to refer to detected compounds as 'lipids' or even 'lipid like'). While I defer to the authors, my preference would be to avoid using such classifiers that aren't particularly relevant to the sample at hand.

Response: We agree with the reviewer that descriptive terms for areas in VK diagrams should be treated carefully, however the authors consider it helpful to use the terms, when implemented in broader context, to help readers that are not as familiar with VK diagrams. As in this paper the term lipid-region is accompanied by the detailed description of what kind of compounds are found in this area (H/C > 2, low O/C, low aromaticity, low carbon oxidation state) it should be sufficiently clear to the reader.

Page 8 Line 39: While true, this statement in and of itself is not novel. To be fair, the authors aren't saying it is https://pubs.acs.org/doi/full/10.1021/acsearthspacechem.1c00141, the same as referenced above) which have similarly shown the utility of a multi-modal assessment of wildfire particles.

Response: We agree with the reviewer and have added the mentioned reference as well as changed the sentence to more clearly state that this is part of the justification and motivation to use different ionization techniques.

Page 9 Line 9-10: The authors should clarify that by 'the highest abundant compound class,' they are referring to the class with the most assignments. Although it is likely that the CHO class also has the highest actual abundance, it cannot be definitively stated using uncalibrated MS data.

Response: We agree with the reviewer and have changed the sentence to be more precise.

Page 9 Line 16: Point the reader to a particular figure.

Response: We have added a reference to Figure 4b.

Page 9 Line 17-18: If a reference to 'the literature' is made, then it should be supported with appropriate references.

Response: We agree with the reviewer and have added specific references.

Page 10 Line 21: What is meant by 'most frequently detected'? Surely CHO compounds were detected in every sample too, so it isn't clear what this statement implies.

Response: The CHNO class showed the second highest relative intensity but the highest relative number of the compound classes. We have changed the sentence to be clearer.

Section 3.3.4.: If the potential contamination concerns outlined in a previous comment are true, then the authors should very carefully consider whether the peaks discussed in this section are truly endogenous to the sample, or perhaps an additional contamination artifact.

Response: We agree with the reviewer that possible contamination need to be considered during the discussion. However, as discussed in more detail in a previous comment, the blank correction with a field blank was carried out for all samples. Also, compounds discussed in this section are most or uniquely found in the wildfire impacted samples. Therefore, there is a high certainty that these CH and CHN compounds originate from the wildfire and not from contamination.

Page 12 Lines 11 – 22: Direct the reader to Figure 6 at some point here.

We agree and have added a reference to Figure 6 to the text.

Page 13 Lines 14 – 16: While the correlations shown in Figure 6 appear to indeed show a trend, I caution against using this data in the current tone. Again, the authors do indeed seem to show a trend. But given that uncalibrated MS data is inherently not quantitative, that there is likely isomer effects, etc., multiple additional caveats needed to be stated before this data can be shown. The authors state in the SI that 'As REMPI is conducted under vacuum conditions, the intensity of an analyte is linearly proportional to its concentration in contrast to direct injection of samples and ionization under atmospheric pressure conditions, such as ESI or APPI.' This is not entirely true in its current wording, as MALDI and LDI (both vacuum based techniques) are well known to exhibit matrix effects. In summary: while the authors present the data interpretation in a way that may be appropriate to the study at hand, the implications should be clarified to better include caveats and need for calibration.

Response: We thank the reviewer for bringing up this topic. With the use of moderate laser fluences (in the order of 10^7W m^{-2}), REMPI is in fact a quantitative technique (Boesl, 2000) and gives linear responses with increasing concentrations with a response factor known as photoionization cross section. (Gehm et al., 2018; Miersch et al., 2019) Like any other analytical technique, REMPI-TOFMS suffers from more than one analyte contributing to the same channel (i.e., *m/z*), which also cannot be solved by calibration. However, due to its high ionization selectivity, the number of possible interferences is even rather limited compared to other techniques.

The statement about linearity and comparison to AP techniques was intended to relate to the ionization techniques used in this study. When the pressure in the REMPI ion source is increased, it is shifted to medium- and atmospheric pressure laser ionization (MPLI/APLI). In this comparison, our statement remains correct as matrix effects and non-linear responses between signal and analyte concentration occur.

REMPI is a gas phase ionization technique, whereas LDI and MALDI are used for solid samples. Therefore, "vacuum condition" refers to a different meaning. During the ionization in MALDI and LDI, a plume from volatilized solid samples is generated with mean free path between molecules, atoms and ions shorter than in our REMPI ion source. Otherwise, no charge transfers could occur, which is the main mechanism for these techniques. Although MALDI/LDI can be carried out under vacuum conditions in terms of sample environment, the ionization does not take place under such. Considering the meaning of vacuum conditions, our statement remains generally true because due to the inverse relation between pressure and mean free path of particles during the ionization, no interactions between particles (ions, atoms and molecules) are possible.

Page 14 Lines 22 – 23: This statement (the link to proteins) needs to be referenced.

Response: We believe that the reviewer refers to page 15 Lines 22-23. We have added a reference for the statement. (Fuentes et al., 2010)

SI: The choice of a 1-1 methanol:dichloromethane mixture is interesting on the basis of comparison to other wildfire studies. The authors should comment in the manuscript that their chosen solvent conditions are more likely to bias the extraction to non-polar constituents. Can the authors also comment on their ESI spray stability after using such a high concentration of DCM?

Response: We agree with the reviewer that the chosen solvent mixture of MeOH/DCM is useful for the comparison to other wildfire studies. The authors consider this solvent mixture to be a broadband extraction that is able to extract polar as well as non-polar compounds. The selection of e.g., water or only methanol may slightly enhance the extraction efficiency of highly polar compounds, but as was shown in this study, highly polar compounds (e.g., CHO16, Figure S12) are also extracted by the chosen solvents.

The ESI spray stability was not negatively affected by the portion of 50% DCM. It was made sure that the ESI spray is stable before each measurement was started.

SI: were radicals allowed for in the APPI assignments?

Response: Yes, radicals were allowed for APPI assignments. We have added this to the text SI.

SI: Were blank mass spectra recorded? If so, how were they accounted for in data processing?

Response: Yes, field blank and solvent blank mass spectra were recorded and used for blank correction by deletion of signals in the blank spectrum from the spectra of the filter samples. As discussed for previous comments, an explanation of this was added to the text.

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