

This measurement report by Jokinen et al. quantifies the seasonal and monthly variation of the important aerosol precursor gases sulfuric acid (SA), methane sulfonic acid (MSA), iodic acid (IA), and highly-oxygenated organic molecules (HOMs) from the remote field station SMEAR I in Värriö Northeastern Finland. The chemical species are measured almost constantly by a state-of-the-art nitrate chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-APi-TOF-MS) in the period between April-October 2019. In addition, the authors link the four chemical species and their seasonal concentrations, as well as meteorological parameters to new-particle formation (NPF) events classified by a Differential Mobility Particle Sizer (DMPS) and a Condensation Particle Counter (CPC).

The overall measurement reported is of good quality and its presentation is well structured, while the language is for the most part precise and fluent. As the authors mentioned, these are the first long-term measurements in a sub-Arctic region that can help the scientific community to understand regional chemical processes and formation of atmospheric aerosol as well as their dynamics in this remote region that is very sensitive to the Earth's rapid climate change. The scientific methods and assumptions are valid, and the interpretation of the measured data is discussed in detail, while the conclusions are limited and not always entirely clear. The conclusions therefore rather give a rough overview of the detailed mechanism of new-particle formation in sub-Arctic areas. As a measurement report, however, this work provides some interesting insights and serves as the basis for future and expanded research in this region. Since there are no major scientific concerns, I believe that this manuscript can be published in ACP as a measurement report after addressing the following mostly minor comments.

We kindly thank you for your time to review our manuscript and giving valuable comments how to improve it. We give you our detailed reply in the following sections in blue text.

***Minor comments:***

1. line159-61: Does this LOD of  $4 \times 10^4 / \text{cm}^3$  also applies to other species than SA?

Yes, it does, the instrumental background is used to count the LOD and it is at the same level for all the individual compounds in this study.

2. line197-99: Does these heatwaves have a substantial impact on the NPF at this site? Can the authors elaborate a little more on this in the discussion part as this may more often in the future?

The increasing temperature will increase VOC emission and collaterally their oxidation to HOM will likely be emphasized with the current level of oxidants. However, heat wave conditions are (likely) not favourable conditions to NPF since condensation of low-volatility gases is favoured in colder temperatures (via the vapor pressure decrease with lower temperatures). Thus, heat waves could possibly inhibit NPF at the current precursor concentrations. However, if the VOC emissions leading to HOM concentrations increase, the growth of particles might be enhanced. The question remains whether the initial clusters are stable enough to reach that diameter where HOMs start to grow them even further or if pure biogenic nucleation (formation of dimers seems more plausible in hot conditions) could take a role in NPF during the heat wave periods in the future. Interestingly, the new figure plotted for Ref1 shows that the HOM concentrations seem to level above ca. 18C.

We added the following sentences into the discussion (chapter starting from line 197):

However, heat wave conditions are likely not favorable conditions to NPF since condensation of low-volatility gases is favored in colder temperatures (via the vapor pressure decrease due to lower temperatures), but they may affect the oxidation chemistry of VOCs by promoting dimer formation.

We also added a figure of the temperature dependence of HOMs in the manuscript and added some words (underlined) to a sentence (line 340): “It is striking how well the concentration of HOMs follow the air temperature (Figure 5) but seem to level above circa 18°C.”

3. Figure 2: Since anthropogenic pollution plumes from the nearby smelters also affect the SMEAR I site, mixing ratios of SO<sub>2</sub> and NO<sub>x</sub> should be added here, if available, like it is done in Sipilä et al. (2021). This can help to understand various aspects of the photochemistry at this location (e.g., types of radicals and quantitative estimation, such as OH, NO<sub>3</sub>, RO<sub>2</sub>) and to separate NPF events from biogenic and anthropogenic sources.

We modified figure 2 to include more trace gas data, including NO<sub>x</sub>, SO<sub>2</sub> and ozone. We decided to depict NPF days in two of the subplots to guide the eye, plotting NPF events on every panel made the figures look too crowded. We also added NPF dates in Figure 1 panel D. We hope that is sufficient for the reviewer.

4. line239-41: Why does the missing March data make the comparison (*more*) uncertain and in what perspective/direction. Can the authors elaborate on how far the diurnal cycle (e.g., peak concentration) or the overall SA concentration might change?

The missing data from spring (1 March – 3 April) equals ~30 % of the data allocated to spring data.

We added the following in the text:

“The SMEAR II data set that includes March data cannot be expected to be perfectly comparable with our data. However, as reported by Sipilä et al., 2021 the March data from the following year seems very similar concentration levels what we report in here for spring (max. ~2e6 cm<sup>-3</sup> and daily averages peak around 0.5e6 cm<sup>-3</sup>). We expect that the SA concentrations are only marginally affected by the lack of March data, but that the level of HOMs or MSA or IA could be affected more due to very different meteorological conditions between the stations in springtime (SMEAR II is ~700 km South from SMEAR I). “

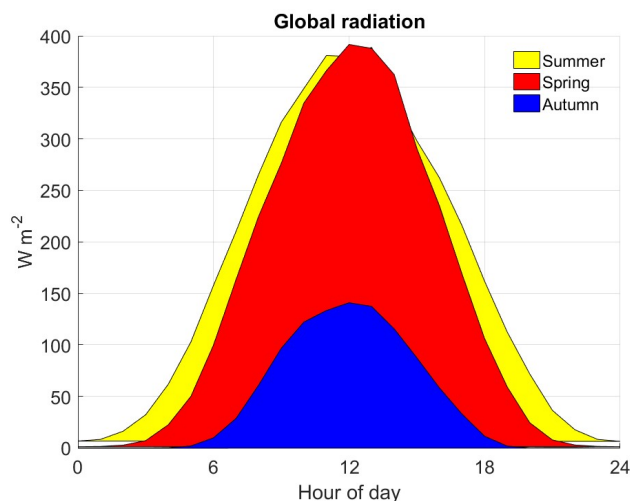
5. line243-53: Is there NO+NO<sub>2</sub> mixing ratios available during this period to state whether the HOMs at SMEAR I are mainly non-nitrate HOMs or organonitrates? This difference can also have a strong impact on HOM dimer formation and thus on NPF at this site. Taking the sum of HOMs (non-nitrate and organonitrates) from Sulo et al. (2021) at SMEAR II would result in a comparable diurnal cycle of total HOMs to SMEAR I. Sulo et al. (2021) shows a clear peak of organonitrates in summer at midday around 1x10<sup>7</sup> mol./cm<sup>3</sup> while the non-nitrate HOMs are at ~ 0.4x10<sup>7</sup> mol./cm<sup>3</sup>. In the evening non-nitrate HOMs increase to about 0.8x10<sup>7</sup> mol./cm<sup>3</sup> while the organonitrates begin to decrease but remain almost at the same concentration as the non-nitrated HOMs. It would be easier to follow the discussion and improve the reader's understanding of the various chemical species to include this section on HOMs in the later section starting at line 314.

The CI-API-TOF data can be used to separate between nitrogen containing and other HOMs without the NO and NO<sub>2</sub> data (which are available from smartSmear). However, the scope

of this manuscript is to give an overview on the data, not to go into details of HOM chemistry. We acknowledge the fact that the data set could have been used to interpret HOM chemistry and its connection to NPF events in more details, but we decided that those will be discussed further in another separate manuscript in the future.

6. Figure 3: It might be useful to add the diurnal cycle of the global radiation from the different seasons within the plots to link the aerosol precursor gases production to the ongoing photochemistry at SMEAR I station.

The global radiation is now depicted in panel 3E with the following addition in the caption; Panel E depicts the seasonal variation of global radiation. The small (false) offset (6-7  $\text{W m}^{-2}$ ) in summer data is due to 24 h sunlight at Värriö.



7. line314-16: Is the sum of HOM concentration in Yan et al. (2016) similarly calculated to this study (summation between 300-600 Th) and corrected for transmission to be comparable? Please add Yan et al. (2016) to the reference list.

In Yan et al., 2016, they used the mass range of 201–650 Th as the total HOM concentration. We choose to use 300 Th as the lowest value due to peaks between 200-300 Th including e.g. one charger ion peak ( $(\text{HNO}_3)_3\text{NO}_3^-$  at 251 Th), iodic acid cluster ( $\text{HNO}_3\text{IO}_3^-$  at 283 Th) and a persistent peak at 201 Th that is identified in Yan et al., 2016 in the transport factor. Those peaks would have distorted the HOM sum data reported in the manuscript.

We do recognize that this sum of HOMs is not an ideal way to represent the complex HOM data set. However, this manuscript is meant to give the reader an overview of the data and to depict the abundance of HOMs (as group of compounds) at SMEAR I.

Figure 5: I would also recommend plotting HOM concentration on the x-axis and temperature on the y-axis while coloring the global radiation. This might also reveal whether the behavior is linear or else. Does one data point represent a daily mean?

We added the requested plot in the manuscript (see answers to Reviwe #1 also). One data point represents 30-minute average, in total this figure has 4960 data points.

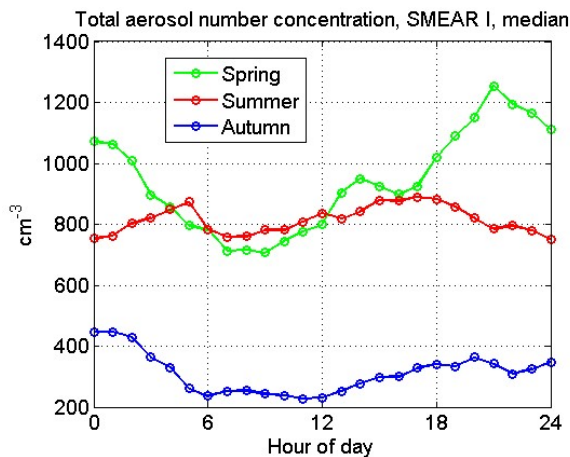
8. Figure 6+7: Since there is a clear seasonal (and even monthly) variation in aerosol precursor gases concentration, I wonder if this also leads to a diurnal variation of NPF events.

Therefore, a more distinct seasonal (or monthly) profile of median number size distribution and total particle concentration of the NPF events here would be more meaningful in my opinion.

Panels B and D in figure 2 are now updated to have NPF events that to cover the whole measurement period. It can be seen that spring is most abundant time for NPF to occur and that there is a long period during late summer (from mid-July to early-Sep) where only one NPF is observed. The whole period has only 33 events all together (2 type 1A-event, 11 type-1B events and rest were type 2 events). Thus, the monthly or even seasonal would have ended up having just a few events and we thought it would be best to group them all together.

The seasonal variation on  $N_{tot}$  is plotted below and we added it with Figure 3 as panel F), hoping that this is satisfactory for the reviewer. The plot is showing the lower concentration in autumn and the impact of NPF in the spring as increase in  $N_{tot}$  in the afternoon and evening. We added a sentence to chapter 3.2. (5<sup>th</sup> row) to explain the figure shortly:

“We detect an increase in total aerosol number concentration on the spring evenings that is likely due to more frequent NPF events taking place at SMEAR I”.



- line364-71: The authors may add distinct numbers to the temperature, RH, and global radiation differences between event- and non-event days, as was done for the ozone concentration.

Text was edited as following;

“In Värriö, NPF events preferably happen in relatively low temperatures (1 – 8 °C) with a fast temperature rise in the early morning hours, lower and decreasing RH, dropping from 90% to ~55 %, during the NPF days compared to non-event days. NPF days have clearly higher global irradiance values (~450  $\text{m}^{-2}$  vs. ~200  $\text{m}^{-2}$ ) and about 10 ppbv higher ozone concentrations than non-event days.”

- line384-87: To what extent are the boundary layer dynamics affected during the day; especially concerning sunrise and sunset during the different seasons. What influence does it have on the measured precursor gas concentrations?

For an accurate assessment of the contribution of secondary aerosol formation to larger aerosol particles, the meteorological situation, including boundary layer dynamics, wet

deposition of particles, etc. should be considered. Sipilä et al., 2021 (ACP) reports that the SO<sub>2</sub> concentrations are likely be much larger due to smaller PBL in winter time and thus, less mixed in the PBL. It is difficult to estimate the PBL effect on NPF without measurements at the site, thus we consider this something to develop in the future at the SMEAR I.

- line391: Since the concentration of the measured gases depends on the wind direction and the air masses exposed to sources of volatile precursors, it would be great to add the wind direction to Figure 1.

We also thought of that and the figure we plotted is attached in here. It did not seem to give any essential information that we wanted to focus on in this article. We also thought to plot windroses (attached) but in the end, we decided go for the cluster analysis of air masses (Fig. 11) as we feel is the best way to see where the airmasses originated during the events vs. non-event days.

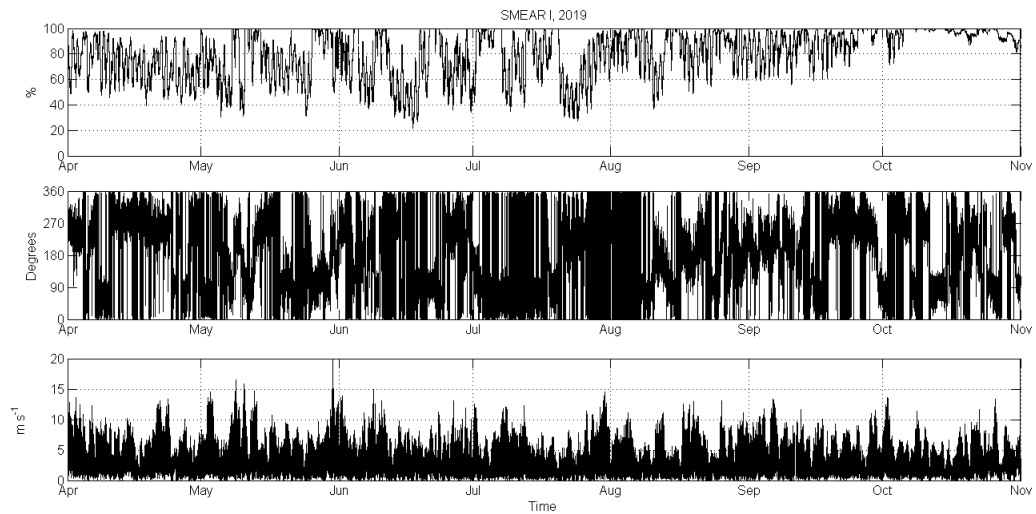


Fig i) SMEAR I meteorological parameters, RH % (top), wind direction (middle) and speed (bottom).

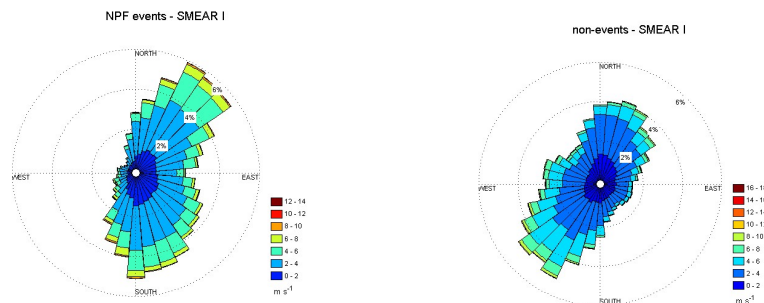


Fig ii) Windroses, NPF events on the left and non-events on the right.

- line394-401: It looks like the air masses of cluster3 of event days and cluster2 of non-event days passed over the highly polluted region of Kola Peninsula. A representation of the

average particle number size distribution as a function of the different air mass clusters could therefore be very helpful here. In addition, as noted by Reviewer 1, the values of the condensation sink and the coagulation sink of small particles are important parameters for the classification of NPF events that should be added to the manuscript.

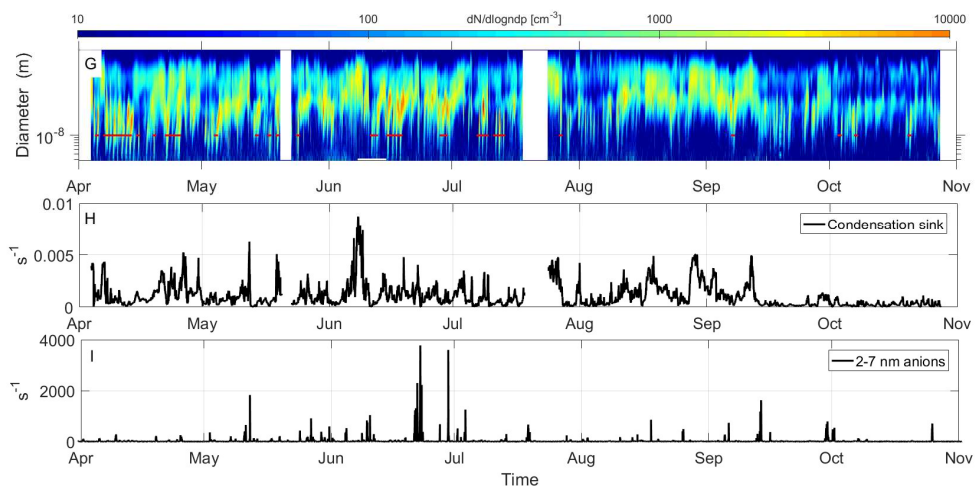
As reviewer no 1 also suggested, we added condensation sink to the manuscript. It can now be found in Figure 2H for the whole measurement period. The figure can be found below also.

The note of the air mass clusters we answer that many previous studies already report that Kola emissions contribute to elevated SO<sub>2</sub> mixing ratios, particle formation events and particle numbers at the site (eg. Sipilä et al., 2021, Kyrö et al., 2014, Vehkamäki et al., 2004). Since the focus of this article is in the overview of aerosol precursor vapours, we did not see it necessary to plot the particle number size concentrations as a function of the clusters.

As suggested by both reviewers, we added the condensation sink in figure 2 from the whole measurement period, the figure is attached below.

- Chapter 3.3: It would be helpful to have an overview showing the aerosol size distribution, wind direction, concentration of small particles or 2-7 nm negative ions, the particle sinks, and the NPF events over the entire measurement period, similar to Figure 2 in the accompanying article by Sipilä et al. (2021). In addition, the NPF events can be highlighted in Figure 1 and Figure 2 using background shading.

Thanks for the suggestion, you are correct. We added more descriptive plots covering the whole measurement period in Figure 2 (addressed earlier) and here (below) is the figure we added to describe the aerosol population and condensation sink for your convenience. The parameters suggested are indeed very necessary for the manuscript. The NPF events are depicted in the DMPS plot in red dots, just to avoid covering the particle size distribution data.



- line409-414: Instead of using the sum of the HOMs, it may be useful to focus only on the ULVOC and ELVOC parts when parameterizing NPF, if possible. As mentioned by the

authors, however, HOM may play a minor role in nucleation, while it can strongly influence particle growth and compete for coagulation losses.

The HOMs are a fascinating subject to research, but as the purpose of this paper is to give an overview of SMEAR I CI-APi-TOF measurements, we do not see this approach necessary here. Thus, the volatility of HOMs is outside the scope of this article. We will definitely look into the HOM composition, its volatility and role in nucleation and growth in a separate manuscript in the future.

15. line415-417: Is there no evidence of mixed clusters between sulfuric acid, iodic acid, MSA, HOM, or possibly bases such as ammonia or amines observed by the nitrate CI-APi-TOF as reported by Sipilä et al. (2021) with the APi-TOF?

The CI-APi-TOF instrumental background ( $\text{LOD} > 10^4 \text{ cm}^{-3}$ ) is much higher than corresponding ion APi-TOF background. We would **assume** that the level of possible SA clusters is very low ( $< 10^4 \text{ cm}^{-3}$ ) like at SMEAR II (Jokinen et al., 2012) and thus not detected at SMEAR I. Since the detailed NPF mechanism is out of this manuscript's scope, we will leave this as an open question to solve.

16. To maximize the information provided in the abstract, please include unambiguous numbers of aerosol precursor gas concentrations and measured values rather than relative descriptions (e.g., “MSA shows a more distinct seasonal cycle with concentrations peaking in the summer of about  $1 \cdot 10^8 \text{ mol./cm}^3$ ”; or: “under relatively low temperature (1-8 °C)”). Why is the significant higher global radiation on NPF-event days not mentioned in the abstract?

Thank you for the suggestion, we added measured values into the abstract to make it clearer. It now reads:

“New particle formation events at SMEAR I happen under relatively low temperatures (1 – 8 °C) with a fast temperature rise in the early morning hours, lower (55% vs. 80% minimum value) and decreasing RH during the NPF days compared to non-event days. NPF days have clearly higher global irradiance values ( $\sim 450 \text{ m}^{-2}$  vs.  $\sim 200 \text{ m}^{-2}$ ) and about 10 ppbv higher ozone concentrations than non-event days.”

### ***Technical corrections:***

1. Please add the numbering of the individual chapters according to the text. **Done.**
2. Some passages require language editing. **We did our best to edit the language.**
3. line170: [...] were downloaded [...]? **Fixed to “were”.**
4. line247: missing space between ‘are one’. **Fixed.**
5. line298: missing ‘t’ in events. **Fixed.**
6. line336-337: “[...] and detected aerosol precursor gases during NPF days [...]” **Fixed.**
7. Figure 6: In the figure caption there is a ‘during’ too much. **Second “during” deleted.**
8. line369: “The meteorological conditions that favor NPF are thus similar to those at the SMEAR II station in Hyytiälä, [...]”. **Fixed.**

9. line377: Where does the reference 'Kulmala et al. (2013)' belong to? Furthermore, in this line add a 'C' to figure reference (e.g., Figure 8C). ~~Kulmala~~ deleted and "C" added.
10. line467: SMEAR III? *Typo fixed.*
11. The short summary needs to be revised in the second sentence.