We thank the anonymous reviewers for their valuable feedback and constructive criticism that have helped us to revise the manuscript. Here we provide answers to their comments and explain how the manuscript was revised following their suggestions. Our answers are in red color and the original comments in black.

The biggest change in the manuscript is moving from three size classes to two size classes following the recommendation by Reviewer 2. Therefore, the figures, tables and text have been revised throughout the article to represent these two size classes. We think the change has made the article easier to follow.

Interactive comment on "Long-term measurement of sub-3nm particles and their precursor gases in the boreal forest" by Juha Sulo et al.

Anonymous Referee #1 Received and published: 5 September 2020

In this manuscript, five years of sub-3 nm particle concentrations obtained with the PSM and three years of precursor vapor concentrations measured with the CI-APi-ToF at the boreal environment are presented, and possible correlation between particles and vapors are examined. This is a unique dataset analyzed and the results are definitely worth being presented in ACP after few minor revisions.

A general comment is the presentation of variabilities of the various atmospheric constituents' concentrations. After the presentation of the full data series for both particles and vapors I would like to see a summarizing Figure for the annual variability of each parameter so that the reader can have a direct impression about the seasonality observed. With regard to diurnal variabilities presented, I recommend normalized rather than absolute values to be used. Additionally, tables with descriptive statistics should C1 be included.

As per the reviewer's suggestion, we have added annual variability figures for both data series and added a summary table of descriptive statistics. We have also changed the diurnal variability figures so that each particle size range and vapor has its own figure in linear scale, allowing the reader to observe the diurnal patterns clearly while keeping the absolute values. We feel that comparing the absolute values from the figures at a glance is an important part of the figure. This also answers the comment by reviewer 2.

Specific comments:

Line 169: The red plusses do not contribute to this Figure, they look rather as an apparent red line. A table summarizing what is shown in Figure 2 would be more helpful to understand how much data was eventually excluded from the analysis. What is the benefit from dividing the data in these three categories eventually?

We have excluded the outliers (red plusses) from Figure 2 and added a table to summarize the amount of data in each category. The reasons for dividing the data into these categories are detailed in L170-180 "When the background is under 1 cm-3, the measured concentrations are on average lower than when the background level is above 1 cm-3, indicating that we are not activating all of the 1.1 - 1.7 nm particles at those settings. However, if the background level rises to over 10 cm-3, also the variation becomes notably larger, underlining the various factors affecting the concentration at higher background. At high background levels the PSM likely activates large vapor molecules or clusters whose concentrations are not stable, leading to larger variation in the concentration. When these species dominate the activated particles, the particle size distribution cannot be easily resolved from the scans.."

Line 213: Does the comparison with the NAIS refer to the whole measuring period included in this study? If so, what changes for the different instruments used?

No, it does not, as the neutral PSM needed for this analysis was only available from 2017 to 2019. Added the line "The ion concentrations were acquired from a PSM with an ion trap inlet (Wagner et al., 2017, Kangasluoma et al., 2016a) <u>measuring in the same container as the long-term</u> <u>measurement PSM. The neutral PSM data was measured between April 2017 and April 2019</u>."

Line 325: In Figure 2 the tick marks of the months suggest an earlier start of the season (is it because the mark is set for the mid of the month?).

We assume the reviewer means Figure 4 in this comment. The ticks for the boxplots are set in the middle of the month. Clarified the caption by adding the line "The tick marks visible are in the middle of the starting month for each season."

Line 348: The discussion of Figure 5 is not clear to me. In all data figure, 1.3-1.7nm do not show any variability. 1.1-1.3 nm present a clear maximum in the evening, but only a weak maximum at noon. 1.7-2.5 nm show a clear minimum during night-before sunrise, higher concentrations during the day and maximum values during the evening. I recommend for all diurnal patterns and given the seasonality presented in Figure 6 to present normalized diurnal patterns so that these variabilities become more evident. I also think that there are extremely low values at 00:00 especially for the 1.3-1.7 nm mode that need to be double checked, the rapid drop at NPF days might result from not valid data-it definitely looks weird.

We changed the diurnal pattern figures to include one size range per figure in order to better observe the diurnal variation and maximums and minimums. We also changed the data to only two size bins as suggested by reviewer 2 to reduce the uncertainty from the sizing in the inversion. The data points were also double checked. Following these changes, we revised the text discussing Figure 6 (old Fig 5.).

Line 380: No, it does not, there is a single maximum in the evening. Once again I recommend normalizing the values, so that any variability becomes more evident.

This has been amended in the text: "We observe a maximum for the 1.1–1.7 nm concentration in the evening and a second smaller peak in the afternoon."

Line 385: It looks quite similar to spring to me. A table with statistics of the various concentrations described would be most helpful for the reader to understand the variations described.

We have added a table with descriptive statistics of both particle and vapor concentrations.

Line 407: I see a lot of outliers for high values but none for low values. Once again the pluses are not contributing to the discussion of the Figures, they are rather confusing. C2 To me, there are pluses that are within the 95th percentile, it has to be clearer.

We have clarified the figure by removing the outlier values from the figure to clarify the discussion.

Line 419: Once again I believe that normalizing the data will produce much better Figures. Additionally, the authors could consider presenting in the same figure the various vapors to assist the eye to identify the variations during the various seasons. We have elected to represent each vapor in its own figure to better allow a comparison between different seasons and between NPF and non-event days and changed the scale from logarithmic to linear. We believe the figures are much clearer now.

Line 421: Figures 8 and 9 are mixed up, 9 comes before 8, probably in the text as well.

This has been corrected and the Figure 8 now comes before Figure 9. The numbering of the figures has changed due to the annual variation figures added to the manusctipt.

Line 459: It does not look that "sharp".

We have rewritten this section to be more synthetic and it does not describe the peak as sharp anymore.

Line 462: Tables with descriptive statistics will provide the reader a more quantitative perspective of the Figures.

A table of descriptive statistics depicting the medians and the 25th and 75th percentiles has been added to the manuscript (Table 3).

Line 505: This is true for the event periods. However, it is worth mentioning that all vapors have statistically significant correlation with the lower size bins for all data, which implies that these vapors play a significant role in the formation of clusters.

The new results from splitting the data into two size bins have changed these results, and although the results still show a statistically significant correlation, the correlation coefficients themselves are lower. This is likely due to other dynamics included in the lowest size bin due to its expansion. We added a sentence saying: "Particle concentrations show positive correlation with all the measured precursor vapors, but we can see slight differences between the two size ranges and between NPF event times and the whole data set."

Line 546: What about the correlations described earlier, are they logarithmic as well?

Yes, they are. This has been checked and the term logarithmic added to appropriate sections when the correlations are mentioned.

Line 552: HOM Nitrate dimers.

Added the word "nitrate".

Technical corrections:

Line 39: "in the atmosphere" repetition.

Removed the repetition.

Line 43: Period before "Studies".

Added a period.

Line 144: Period mark repetition.

Removed the repetition.

Line 144: Is it perhaps "thought" rather than "though"?

The reviewer is correct. This has been amended.

Line 301: It should be Table 1.

Corrected to "Table 1".

Line 508: Remove paragraph.

Paragraph removed.

Line 558: Remove "correlations".

Removed "correlations".

Reviewer 2:

The paper by Sulo and co-workers presents long term measurements of sub-3 nm particle concentration and their precursors conducted in Hyytiälä, in the boreal forest. The first part of the study focuses on the identification of optimal settings of the PSM (used for particle measurement) for this site. The second part is dedicated to the study of the time series, including diurnal cycles, of the gas and particle concentrations. The involvement of the selected vapours in the formation of sub-3 nm particles is finally addressed in a last part by the mean of a correlation analysis.

While the data set used is of undeniable value and the objectives presented are of obvious interest, I am however reserved on certain aspects of this study. My main concern is about the definition of the particle size classes used for the analysis, which seem to me too fine in view of the uncertainties associated with the measurement, with a probable impact on the results presented, and in particular on the correlations. Moreover, it is sometimes difficult to extract the main messages from the second part of the study, which is very descriptive, and which I believe would benefit from being sometimes more synthetic. The integration of a more "chemical" dimension to the analysis proposed in Sect. 3.2 would finally, in my opinion, make this second part more complete. These different aspects are presented in more detail in the comments listed below, which I think should be considered before publication of this work.

P2, Introduction: measurements performed in Hyytiälä have enabled numerous studies to be carried out, in particular on the understanding of new particle formation and the identification of its precursors. I would thus suggest to include in the introduction a paragraph recalling some key results specific to this site in order to better situate the objectives and interest of this new study in relation to past work.

Good suggestion. Added a short paragraph recalling some of the key results from earlier studied from the SMEAR II data into the introduction: "The long-term measurements at the SMEAR II station in Hyytiälä, Finland, have enabled studying atmospheric new particle formation and its prerequisites. Prior research has investigated the frequency of NPF in the boreal forest (Dal Maso et al. 2005; Nieminen et al., 2014) and how it is affected by condensation sink and cloudiness (Dada et al., 2017) and other meteorological conditions (Sogacheva et al., 2007). These studies have

concluded that NPF is most common in Hyytiälä during spring and that NPF occurs most often during days with fewer clouds and a low condensation sink. Shorter campaign measurements have been used to investigate the connection between NPF and its precursors vapors (e.g. Riipinen et al. 2007; Kulmala et al., 2013; Yan et al. 2018). They indicate that both sulfuric acid and some organic vapors participate in NPF in Hyytiälä, but the possible seasonality of the mechanism and exact identity of the organic compounds are still unclear.

P6, L177: The authors indicate the appropriate settings for the station of interest but it is not completely clear to me to which extent these settings are site specific. Could the authors add a sentence or two to briefly comment on these aspects, and discuss in particular the possibility of extrapolating the results obtained to other sites, under what conditions?

We have added a comment on the suitability of these settings for other measurement locations: "The optimal settings determined here can likely be used in measurement sites with similar particle concentrations and composition. However, if a measurement location has much higher particle concentrations or the changes in particle concentration are much more rapid than in a boreal forest, for examples in an urban measurement location, they will have to be adjusted. Also, the composition of smallest particles might affect the ideal level of supersaturation to activate most of them without too much disturbance from homogenous nucleation."

P7, Measurement uncertainties: measurement uncertainties related to the nature of the particles and sampling conditions have been the subject of various studies in recent years and are clearly recalled here. Given these uncertainties, I wonder what is the relevance of size classes as fine as those proposed in this work. In particular, the width of the proposed bins is of the same order or less than the uncertainty related to the chemical composition of the particles or their charge. My interrogations are reinforced by the fact that on NPF event days (Fig. 5), the evolution of the concentrations does not seem to show any growth link between the different classes, or at least between the 2 last ones which are considered to be more connected to NPF. I think it would therefore be more appropriate to reduce the number of classes.

As per the reviewer's suggestion, we have reduced the number of size classes to two - 1.1-1.7 nm and 1.7-2.5 nm. One for the smallest particles with more constant behaviour and one for particles that are clearly connected to NPF. With this new division the growth link becomes very clear in Fig 6: the 1.1-1.7 nm particles start rising on NPF event days a little bit earlier than the 1.7-2.5 nm particles.

P10, L254-256: is the frequency of events of marked stratification known, significant? Should the correlation analysis reported in Sect. 3.3 be limited to day time in the "All data" cases?

According to Alekseychick et al. (2013) ca. 19% of nights show strong stratification (decoupling of the sub-canopy and above-canopy layers) in Hyytiälä. Since it is a minority of data, and because we believe it is important to include the nighttime to get more variability in the concentrations, we decided to include also nighttime into the correlation analysis. Furthermore, we investigated the correlations with the "All data" cases limited to daytime and the difference in correlations was minor (+- 0.05) for all investigated vapors and particle size ranges.

P11, L280-282: "Correlations were also separately investigated for spring- and summertime NPF events. There were not enough data points for events during autumn and winter for separate analysis during those seasons." If I am not mistaken, there are correlations reported for autumn in Table 3.

The reviewer is correct and this has been amended in the text: "Correlations were also separately investigated for spring- and summer- and autumntime NPF events."

P11, L286: Could the authors add a few words on the value of distinguishing between nitrates and nonnitrates?

We have added a sentence explaining the value of distinguishing between nitrates and non-nitrates: "The molecules were divided into nitrates and non-nitrates because nitrate HOMs typically have a higher volatility than non-nitrate molecules (Yan et al., 2020) and it is possible that their contribution to NPF is different (Lehtipalo et al. 2018)."

P12-13: Time series of the particle concentration:

 \Box L320-321: "We observe a clear annual maximum during late spring and early summer". I would say that this statement is too strong since it seems to me that it is only verified for 2 years (2016 and 2018). In 2015 and 2019, the concentrations measured in autumn are of the same order as those measured during late spring / early summer, and in 2017, despite the lack of data, it seems that the autumn levels are even higher than those of the previous months.

We have removed the word "clear" from the statement and added a figure to better illustrate the median annual variability.

 \Box L324-332: "Excluding this part of the data did not have a significant impact on the rest of the analysis." Does this mean that the data were effectively excluded for the rest of the analysis?

The data was not excluded, this was just a test. For clarity, this sentence was deleted entirely, since we did not end up excluding this part of the data.

 \Box L336-337: "and because their data was not filtered to remove scans with too high background". The difference in concentration between the two studies is relatively large (almost an order of magnitude), and I am not sure that the proposed hypotheses can explain such differences. In particular, Fig. 1 suggests that scans with a high background are not systematically associated with higher concentrations than those associated with lower backgrounds (or is it only true for the smallest particles, i.e. in the class 1.1-1.3 nm ?). Was the background itself subtracted from the data in Kontkanen et al. (2017)? Also, I think that based on the studies by Lehtipalo et al. (2014) and Cai et al. (2019), it cannot be excluded that the use of methods other than Kernel (e.g. step wise) could have contributed to the observed differences as well; however, unless I am mistaken, the inversion method used by Kontkanen and co-workers is not specified in their paper.

Figure 1 shows the fraction of bad scans and does not appear to suggest what the reviewer is saying. Assuming that the reviewer is referring to Figure 2, we still see a higher portion of high concentration values in scans with high background, even if they are not systematically associated with those high background scans. we have specified a further reason in the text – in that Kontkanen et al. (2017) subtracted the background from the data manually – and the background measurements were conducted manually (and thus less frequently), resulting in a possible underestimation of the background. However, the exact reason for the difference is not clear and might be a combination of true variability between years and technical reasons. Considering that the uncertainties in sub-3nm measurements (especially in the detection efficiency of neutral particles) are still significant, the most important aspect in this study are not the absolute concentrations but the diurnal and annual variation in different size classes and correlations with the precursors.

P14-15: diurnal cycles of the cluster concentration

 $\hfill \Box$ The use of a logarithmic scale makes the identification of certain maxima / minima very difficult!

This has been amended and the diurnal cycle figures are now in linear scale.

 \Box L369-372: I do not think that the peak observed on event days around noon in the size range 1.7-2.5 nm can be described as a strong maximum. On the other hand, the link between these observations and the occurrence of regional NPF events does not seem obvious to me either; I would expect in this case a chronology in the increase of concentrations (i.e 1.3-1.7 nm and then 1.7-2.5 nm) that is not seen here. Is it also possible that this unexpected chronology is linked to measurement uncertainties / definition of the size classes?

The reviewer is correct that the unxpected chronology could be due to the definition of the size classes. We have reduced our size classes to two in order to reduce the uncertainties in the sizing.

P16: diurnal cycles of the cluster concentration in each season \Box The end of this section is very descriptive, with observations that are often difficult to confirm due to the logarithmic scale (e.g. L389), and it is globally difficult for me to extract a message from this analysis. I would suggest to add one or two sentences at the end of the section to summarize the main outcomes. \Box Concentration levels and the presence or absence of distinctive diurnal cycles are primarily related to the frequency of occurrence of NPF in each season. However, this explanation does not seem to be sufficient, since although the frequencies of NPF are lowest in winter, the concentrations observed are on average higher than those in autumn for the 2 size classes 1.3- 1.7 and 1.7-2.5 nm, and comparable or even higher than those in summer for the class 1.3-1.7 nm.

The seasonal diurnal cycle section has been rewritten to be more synthetic. The differences in concentration are more visible, and the winter concentrations are the lowest. We have also added text to explain the evening maximums.

P17-20: Time series of vapour concentrations:

□ This section is once again very descriptive, with an analysis that sometimes seems too superficial to me. It would, in my opinion, benefit from being more detailed from a chemical point of view, particularly with regard to the processes involved in the formation/transformation of the organic compounds of interest according to their nature (monomers vs. dimers, nitrates vs. non-nitrates) and their influence on the cycles observed. The findings of studies previously dedicated to the specific analysis of cluster composition at the site (e.g. Yan et al. 2016; Bianchi et al., 2017; Rose et al. 2018 and connected literature) could for instance be explicitly mentioned to benefit the interpretation of the results.

We have added more interpretation from a chemical point of view, speculating about the sources of HOM monomers and dimers as well nitrates and non-nitrates.

 \Box L406: "during summer months": based on Fig. 7, it should in my opinion be changed to "between late spring and early autumn".

This has been amended as the reviewer as suggested.

 \Box L445-450: The importance of SA and HOM non-nitrate monomers in the formation and initial growth of the clusters cannot be deduced with such level of confidence from the comparison of median diurnal cycles alone ("This points to the importance", "implying that"). Based on Fig. 5,

the other selected compounds also have variations that are comparable to that of the cluster concentration, and could thus be involved in their formation as well (HOM nitrate monomers peaking around midday, dimers peaking in the evening). I would suggest using more moderate phrasing at this stage of the analysis.

We have amended the language in this section to be more moderate: "During regional NPF event days, the concentrations of all analyzed aerosol precursor vapors are higher than during non-event days (Figure 10). However, the diurnal patterns of the precursor vapors are otherwise rather similar on event and non-event days. The non-nitrate monomers and dimers show a small increase during daytime on NPF days which is absent on diurnal patterns of global radiation in Figures 6 and 9, suggest that during event days there is more photochemical production and potentially also higher emissions of biogenic vapors. However, from the diurnal variations is not possible point out a single vapor explaining the difference between NPF events and non-events."

 \Box L451-487: As in the previous section, I find it difficult to extract the main messages from this relatively long description. I would suggest, for example, to first highlight the fact that the general pattern of the cycles is overall comparable for all seasons, but with amplitudes and/or periods that are variable and probably modulated by the amount of global radiation; I would then describe the main differences observed between each season.

We have rewritten this section to be more synthetic and highlighted the effect of global radiation.

P21-25: connection between precursor vapours and cluster concentrations The search for correlations between the presence of newly formed particles and possible precursors seems to me relevant for the identification of the compounds involved in the formation and early growth process. However, I believe that the uncertainties related to the definition of such fine particle size classes as those used here limit the relevance of such correlation study, whose results are for me difficult to interpret. I still have a few comments on this section:

 \Box L507: I would suggest to better explain the choice of the combinations of compounds to be investigated.

This has been explained in more detail in Chapter 2.5 now with some added detail: ". Laboratory experiments replicating boundary layer NPF in forested regions (Riccobono et al., 2014; Lehtipalo et al., 2018) and previous analysis of field data sets (Paasonen et al., 2010) have shown that particle formation rates can be parametrized using a product of sulfuric acid concentration and organics concentrations. Therefore, we expect that sulfuric acid and HOMs or some combination of them should correlate well with new particle formation in a boreal forest and the correlations in different size ranges might reveal which precursors are most important at different stages of the process."

 \Box L515: "However, the difference in correlation coefficients is not large": It depends on the meaning of large but I would say that the difference is sometimes significant!

We have made the comment more specific with "However, the difference in coefficients is not very large with the uncertainties involved"

 \Box L520-521: "However, the correlation can also point to two separate formation pathways, organic and inorganic." I would suggest to mention the earlier results of Yan et al. (2018) to support the idea of multiple mechanisms.

Added a reference to Yan et al. (2018).

 \Box Fig. 10: Line 494-495 indicates that calibration coefficients are not considered in the correlation analysis, but they seem to be accounted for in Fig. 10. Furthermore, the orders of magnitude shown on the x-axis in the third column (product of the previous 2 columns) do not seem to be consistent with what is shown in the previous columns.

This was indeed an error in the plot, but this has now been rectified and the new Figure shows the data without the calibration coefficients and with the correct magnitudes.

P25-26 : Conclusions Beyond the fact that it remains difficult to approve certain observations due to the use of logarithmic scales, some of the information that is recalled here does not seem to me to be precise enough, or not in line with what is reported in the previous sections:
L592: "The 1.3–1.7 nm and 1.7–2.5 nm particle concentrations show a marked increase during springtime": this is not obvious for 1.7-2.5 nm particles, whose concentration is close to what is observed in summer.

We have softened the language to The 1.7–2.5 nm particle concentration, on the other hand, exhibits the largest median concentration during springtime, coinciding with increased regional NPF frequency." and this is reflected in the Results section as well. The median concentrations are in Table 2.

- L593-594: "The diurnal patterns of sub-3nm concentrations exhibit clear daytime maxima around midday.": It does not seem to be true for all sizes, seasons, types of days (NPF vs non event days).

This has been amended to "The daytime maximum in concentrations is clear during spring, summer and autumn, during which regional NPF events are also more common."

- L594: "This maximum is the clearest during spring and autumn": Barring any misunderstanding on my part, this message seems to me to contradict what is reported in L393-396 regarding autumn: "weak diurnal pattern", "no discernible diurnal pattern".

The new figures present the diurnal pattern more clearly and this is reflected both in the conclusions and in the results.

Technical / Minor comments

P2, L43: point missing at the end of the sentence.

Corrected.

P3, L79: "for measuring particle concentrations larger than 1 nm in size": I would suggest to change to "for measuring the concentration of particles larger than 1 nm in size".

We have changed the sentence to the suggested "for measuring the concentration of particles larger than 1 nm in size".

P5, L144: extra point at the end of the sentence.

Corrected.

P11, L278: extra "then".

Corrected.

P13, L334: "concentration" should be removed at the end of the sentence.

Corrected.

P19, L460: point missing at the end of the sentence.

This paragraph has been entirely rewritten. P24, L558: "correlations" should be removed.

Removed.

Figures: 🗆

I would suggest homogenising, as far as possible, the appearance of the figures and in particular the font size used. Adding a grid would also make the values easier to read.

 \Box Fig. 5: the scale of the ordinate axis (left) of the third panel should be slightly adjusted to match the scale of the others and ease the comparison.

The new figure is easier to read and the concentrations are easier to read.

The writing of times should be harmonized (e.g. L389 vs L424).

Times have all been corrected to the format HH:MM.

References:

Alekseychik, P., Mammarella, I., Launiainen, S., Rannik, Ü., and Vesala, T.: Evolution of the nocturnal decoupled layer in a pine forest canopy, Agr. Forest. Meteorol., 174, 15–27, https://doi.org/10.1016/j.agrformet.2013.01.011, 2013.

LONG-TERM MEASUREMENT OF SUB-3NM PARTICLES AND THEIR PRECURSOR GASES IN THE BOREAL FOREST

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Abstract. The knowledge of the dynamics of sub-3nm particles in the atmosphere is crucial for our understanding of first steps of atmospheric new particle formation. Therefore, accurate and stable long-term measurements of the smallest atmospheric particles are needed. In this study, we analyzed over five years of particle concentrations in size classes 1.1–1.73 nm, 1.3–1.7 nm-and 1.77–2.5 nm obtained with the Particle Size Magnifier (PSM) and three years of-precursor vapor concentrations measured with the Chemical Ionization Atmospheric Pressure Interface Time-of-Flight mass spectrometer (CI-APi-ToF) at the SMEAR II station in Hyytiälä, Finland. The results show that the 1.1–1.73 nm particle concentrations have a daytime maximum during all seasons, which is due to increased photochemical activity. There are significant seasonal differences in median concentrations of 1.3–1.7 nm and 1.77–2.5 nm sub-3nm particles, but the two size classes behave partly differently, underlining the different frequency of new particle formation between seasons. The 1.1-1.7 nm particle concentrations are highest in summer, while the 1.7-2.5 nm particle concentration are highest in springtime. The 1.7-2.5 nm particles have an additional evening time maximum during spring and summer. In particular, concentrations of 1.3–1.7 nm and 1.7–2.5 nm particles are notably

- 25 higher in spring than during other seasons. Aerosol precursor vapors have notable diurnal and seasonal differences as well. Sulfuric acid and highly oxygenated organic molecule (HOM) monomer concentrations have clear daytime maxima, while HOM dimers have their maxima during the night. HOM concentrations for both monomers and dimers are the highest during summer and the lowest during winter <u>following the</u>. Higher median concentrations during summer result from increased biogenic activity in the surrounding forest. Sulfuric acid concentrations are the highest during spring and summer, with
- 30 autumn and winter concentrations being two to three times lower. A correlation analysis between the sub-3nm

concentrations and aerosol precursor vapor concentrations indicates that <u>both</u> HOMs, particularly their dimers, and sulfuric acid play a significant role in new particle formation in the boreal forest. Our analysis also suggests that there might be seasonal differences in new particle formation pathways that need to be investigated further.

35 1 Introduction

Atmospheric aerosols are one of the largest sources of uncertainty in climate models. To diminish these uncertainties, it is vital to understand the sources and formation pathways of aerosol particles. New particle formation (NPF) in the atmosphere has been observed to occur in various environments (Kulmala et al., 2004; Kerminen et al., 2018 and references therein) from megacities (Hofman et al., 2016; Wu et al., 2007; Qi et al., 2017) to rainforests (Wimmer et al., 2018; Andreae et al.,

40 2018), to rural areas (Mäkelä et al., 1997; Vakkari et al., 2011; Heintzenberg et al., 2017; Nieminen et al., 2014) and even polar areas (Weller et al., 2015; Kyrö et al., 2013; Järvinen et al., 2013; Sipilä et al., 2016). In the laboratory, aerosol particles have been observed to form through various pathways involving different chemical compounds and ions (e.g. Kirkby et al., 2016; Lehtipalo et al., 2018). Based on various estimates (Merikanto et al., 2009; Dunne et al., 2016; Kulmala et al., 2016), 40-80% of aerosol particles in the atmosphere are formed from condensing vapours and thus NPF contributes

45 significantly to <u>global</u> aerosol number concentrations.<u>in it.in the atmosphere</u>.

It is widely understood that sulfuric acid (SA) plays a significant role in atmospheric NPF (Kulmala et al., 2006; Riipinen et al., 2007; Paasonen et al., 2010). However, SA and water alone are alone is not enough to explain atmospheric observations in the boundary layer (Chen et al., 2012; Paasonen et al., 2012). Studies indicate that at least one more vapor, for example a

50 base like amine or ammonia, is needed for stabilizing the growing clusters (Almeida et al., 2013; Kirkby et al., 2016; Kürten et al., 2018). Highly oxygenated organic molecules (HOMs), formed in the atmosphere through auto-oxidation from volatile organic compounds, likely partake in particle growth everywhere in the boundary layer (Ehn et al. 2014; Mohr et al., 2019). Some HOMs can form charged clusters on their own, but it is unclear how important these pure biogenic clusters are for atmospheric NPF (Kirkby et al., 2016; Rose et al., 2018; Bianchi et al., 2017).

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Freshly formed particles have typical sizes of 1–2 nm in diameter and they grow to larger sizes by condensation of low volatility vapors (Kulmala et al., 2014). Measuring these sub-3nm particles is critical to a proper understanding of NPF and the early steps of particle growth in the atmosphere. One method of measuring sub-3nm particles is the Particle Size Magnifier (PSM) (Vanhanen et al., 2011). The PSM is a two-stage condensation particle counter (CPC) used to grow and

60 count sub-3nm particles. Sub-3nm particles have been measured with the PSM in various environments (Kontkanen et al., 2017), from polluted Chinese megacities (Xiao et al., 2015) to rural areas (Kulmala et al., 2013) and mountain tops (Rose et al., 2015). Measurement devices are prone to errors, particularly in the field, and understanding the factors that affect the

performance of the PSM and validating data from PSM measurements is an ongoing challenge (Kangasluoma et al., 2013; Kangasluoma et al., 2014; Kangasluoma et al., 2016b).

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The long-term measurements at the SMEAR II station in Hyytiälä, Finland, have enabled studyingseveral studies into atmospheric new particle formation and its prerequisites different properties. Prior research has investigated the frequency of NPF in the boreal forest (Dal Maso et al. 2005; Nieminen et al., 2014) and how it is affected by, the effect on condensation sink and cloudiness on NPF (Dada et al., 2017) and, the effect of other meteorological conditions (Sogacheva et al., 2007)

- 70 and night time cluster formation (Rose et al., 2018). These studies have concluded that NPF is most common in Hyytiälä during spring and that both sulfuric acid as well as some organic vapors participate in NPF. Additionally, they have determined that the NPF occurs most often during days with fewer clouds and a low condensation sink. <u>Shorter campaign measurements have been used to investigated the connection between NPF and its precursors vapors as well (e.g. Riipinen et al. 2007; Kulmala et al., 2013; Yan et al. 2018). They indicate that both sulfuric acid and some organic vapors participate in</u>
- 75 NPF in Hyytiälä, but the possible seasonality of the mechanism and exact identity of the organic compounds are still unclear. These studies have concluded that NPF is most common in Hyytiälä during spring and sulfuric acid as well as some organic vapors participate in nucleation. Additionally, they have determined that the NPF occurs most often during days with fewer clouds and a low condensation sink.
- 80 In this study, we first investigate what are the optimal settings to operate the PSM at the SMEAR II station in Hyytiälä, Southern Finland, to detect sub 3nm particles. Then, we analyze the over 5 year dataset using these optimized settings and analyze over 5-year dataset from the SMEAR II station in Hyytiälä, southern Finland, in order to investigate the diurnal and seasonal variation of sub-3nm particle concentrations in boreal forest and their connection to atmospheric NPF. Additionally, the sub-3nm particle concentrations are compared with some of their possible precursor vapor concentrations in order to
- 85 determine which vapors participate in atmospheric NPF and their relative roles in different size ranges. A secondary goal is to find the optimal settings to operate the PSM in order to detect sub-3nm particles in field conditions.

2 Materials and methods

2.1 Measurement location

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All measurements were conducted at the SMEAR II (Station for Measuring Forest Ecosystem Atmosphere Relations) station in Hyytiälä, Southern Finland (61°5' 0'' N, 24°170' E; 181 m above sea level) (Hari and Kulmala, 2005) between April 2014 and April 2020. Hyytiälä is roughly 200 kilometers from Helsinki, with the closest urban center Tampere about 60 kilometers to the southwest. Tampere has a population of roughly 230 000 people. The SMEAR II station is considered a rural background station for atmospheric measurements and is surrounded by a Scots pine (Pinus sylvestris) forest. The emissions of volatile organic compounds at the station are dominated by biogenic vapors from the surrounding forest, 95 monoterpenes in particular (Rantala et al., 2015). NPF events including particle growth have been observed only during daytime (Buenrostro Mazon et al., 2016), while biogenic cluster formation is common also during evening and night (Rose et al., 2018).

2.2 Particle size magnifier

- 100 We used the Particle Size Magnifier (PSM) to measure the concentrations of sub-3nm particles. The A11 nCNC –system (nano Condensation Nucleus Counter) is a particle counter system developed for measuring the concentration of particles concentrations larger than 1 nm in size and size distributions in the sub 3nm particle size region (Vanhanen et al., 2011). In this system, the PSM operates as a pre-conditioner, in which the small particles are first grown before they are funneled into a CPC for further growth and optical detection. The PSMs used in this study were manufactured by Airmodus (model A10)
- 105 and used together with an Airmodus A20 CPC. In the PSM, the sample flow is turbulently mixed in the mixing region with a saturated heated flow to achieve supersaturation in the growth tube. Diethylene glycol (DEG) starts to condense on the sample particles and they are grown up to the size of circa 100 nm in the cooled growth tube. From the growth tube, the flow is directed to a CPC where the particles are grown with butanol to optically detectable sizes.
- Particle activation within the PSM depends on the supersaturation level in the PSM, which in turn depends on the temperature difference between the heated saturated flow, the sample flow, and the growth tube, as well as the saturator flow rate (Kangasluoma et al., 2016b; Vanhanen et al., 2011; Okuyama et al., 1984). Because of that, the supersaturation can be adjusted by changing the saturator flow rate or the temperature difference between these components. A larger temperature difference between the heated saturated flow and the growth tube or a higher saturator flow rate leads to a higher supersaturation level, which means that smaller particles are activated and thus the cutoff size of the instrument, i.e. the diameter at which 50% of the particles are activated, is lower. However, too high a supersaturation level will lead to formation of droplets via homogeneous nucleation causing a background signal. Studies have also shown that the cutoff size for particles depends not only on the supersaturation, but on the chemical composition of the sample particles, particle charge and the condensing fluid (see Sect 2.2.3.) (Kangasluoma et al., 2016b; Winkler et al., 2012).

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The PSM can be run in several measurement modes, but in this study, we only used the scanning mode. The scanning mode makes it possible to determine the particle size distribution of sub-3nm particles. In the scanning mode, the PSM scans through saturator flow rates to obtain the particle size distribution. In our study, the PSM scanned from 0.1 liters per minute (lpm) to 1.3 lpm and back to 0.1 lpm in four minutes. During the scan, particle counts are saved at a one second interval to

125 the raw data file. Each measurement corresponds to the total concentration of particles above a certain size determined by the saturator flow rate, and therefore the changes in the measured concentration during a scan can be used to acquire information of the size distribution (Lehtipalo et al. 2014).

The PSM measurements were conducted at the SMEAR II station in a container at ground level. Due to maintenance, the instrument was changed on 23 February 2017 and 1 October 2018. In 2014, the sampling was done with a 40 cm long stainless-steel tube with 2.5 lpm flow rate. The diffusion losses were corrected for in the data inversion. From 2015 onward, the sampling was done with the core sampling method, where the air was taken from the outside at 7.5 lpm through a 40 cm stainless steel tube and the sample was taken from the middle of the flow into the PSM at 2.5 lpm to minimize sampling losses. The inlet also included a mechanism which allowed the bypass flow to be briefly reversed in order to provide

particle-free air in ambient relative humidity for PSM background measurements (Kangasluoma et al., 2016ab).

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2.2.1 PSM data analysis

clusters and recently formed particles.

Before the PSM raw data was inverted, the data was run through a quality control algorithm in which we assumed that the measured total concentration during each scan should have a positive and statistically significant (p < 0.05) correlation with the PSM saturator flow rate (Chan et al., 2020). Increasing the flow rate should always result in increased total concentration because we are activating a larger size range of particles. We omitted scans not fulfilling this requirement from further analysis, as they would lead to a negative concentration of sub-3nm particles. These so called "bad scans" could result from air mass changes or other variations in aerosol concentrations that are faster than the scan time, or if the concentration of sub-3nm particles is so low that it cannot be detected with this method.

We inverted the raw PSM data with the kernel method described in (Lehtipalo et. al., 2014) to obtain the size distribution of sub-3nm particles. The kernel method uses a non-negative matrix inversion routine to calculate the size distribution based on activation curves measured during the calibration of the instrument. The data was inverted to a 16-minute resolution (4 scans) and three<u>two</u> size bins (1.1 – 1.<u>7</u>³ nm-1.3 – 1.7 nm, 1.<u>7</u>7 – 2.5 nm) to minimize the effect of noise on the analysis, but still retain a high enough time resolution for the analysis. <u>1.7 nm was chosen as the divider because it is commonly used in studies for nucleation rate calculations (Lehtipalo et al., 2018; Kirkby et al., 2016) and because cluster ions are typically considered to be smaller than this size-as well (Hirsikko et al., 2011). Therefore, the smaller size bin probably consists of
</u>

neutral and ion clusters as well as small recently formed particles, while the larger size bin consists mainly of growing

- 155 Recently, Cai et al. (2019) recommended another inversion routine for PSM data, the expectation-maximization algorithm (EM). However, as our data was already inverted with the kernel method and the EM method is computationally expensive, we decided to stick with the kernel method. The two inversion methods produce similar concentrations and size distributions when both are optimized for the dataset in question (Cai et al., 2019). It remains future work to test the applicability of the EM algorithm for SMEAR II data and optimize it to conditions with rather low particle concentrations.
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2.2.2 Effect of supersaturation and background counts

At optimal temperature settings the PSM should activate a large fraction of even the smallest particles around 1 nm, while still minimizing the effect of homogenous nucleation within the PSM. In practice, a small background from homogeneous nucleation needs to be tolerated at higher saturator flow rates in order to activate the smallest particles, especially organic clusters. The amount of homogeneously nucleated droplets can be taken as an indicator of the supersaturation level (activation efficiency) (Jiang et al., 2011). Here we investigate how the background level affects the measured concentrations.

- To monitor the instrument operation and supersaturation level, the background counts were automatically measured three times a day...day. Due to changes in external conditions and the state of the instrument, the background varies and if the operator thought it was too high (> ca. 50 cm⁻³) or too low (< ca. 1 cm⁻³), the temperature settings were adjusted to keep the cut-off sizes same as before. During the whole measurement period, the daily averaged (over all saturator flow rates) homogenous background varied from less than 1 cm⁻³ to almost a 1000 cm⁻³. The background counts were subtracted from
- 175 the data during data processing.

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We investigated the fraction of scans discarded during data quality control as a function of the background concentrations (daily median) (Figure 1). The u-shape of the bad scan percentage clearly shows that the quality of the scans goes down if the PSM background is either too low (<0.1 - 1) or too high (>10). If the supersaturation level and consequently the background level inside the PSM is too low, the smallest particles cannot be activated and there is no detectable signal,

- which leads to noisy scans. A high background, on the other hand, can indicate that the PSM is not functioning properly. Thus, based on the quality of the scans alone, the PSM appears to work <u>bestmost stably</u> when the background signal at the highest saturator flow rate is between 1 and 10 cm⁻³. However, in our measurements, the devices were never intentionally run at background levels higher than circa 50 cm⁻³. For this reason, the PSM could be stable at higher background levels as
- 185 well, but our data does not allow us to draw conclusions on that. Furthermore, this behavior seems to be uncorrelated with the measured relative humidity at the measurement location, although laboratory studies have shown that RH can affect the particle activation efficiency with DEG (Kangasluoma et al., 2013; Jiang et al., 2011).



190 Figure 1: The fraction of scans discarded during data quality check plotted against the daily medians of PSM background concentration. The color of the circles shows the ambient relative humidity (RH).

To investigate the effect of the background level (supersaturation) on the activation of the smallest particles, we split the data

- 195 points to groups where the background is below 1 cm⁻³, above 10 cm⁻³ or between these two limits. The limits were chosen based on the observed fraction of bad scans in Fig. 1. We then studied 1.1 - 1.73 nm concentration as a function of the PSM background (Figure 2). When the background is under 1 cm⁻³, the measured concentrations are on average notably lower than when the background level is above 1 cm⁻³, indicating that we are not activating all of the 1.1 - 1.73 nm particles at those settings. However, if the background level rises to over 10 cm⁻³, also the variation becomes notably larger bigger and
- 200 the median concentration smaller, underlining the various factors affecting the concentration at higher background. At very high background levels the PSM likely activates large vapor molecules or clusters whose concentrations are not stable, leading to larger variation in the concentration. When these species dominate the activated particles, the particle size distribution cannot be easily resolved from the scans. Other causes for higher variation at high background include but are not necessarily limited to faulty instrumentation, dirty sample lines and dominant homogeneous nucleation of the working

205 fluid.

The analysis described above leads to the conclusion that in the conditions of the SMEAR II station, the optimal settings for the PSM is found when the measured background is between 1 cm⁻³ and 10 cm⁻³. As mentioned before, the PSM could be run stably at background levels above 10 cm⁻³ as well, but due to the results discussed above, we selected for further analysis only PSM data with the instrument background between 1 and 10 cm⁻³. The optimal settings determined here can likely be

210 only PSM data with the instrument background between 1 and 10 cm⁻³. The optimal settings determined here can likely be used in measurement sites with similar particle concentrations and composition. However, if a measurement location has much higher particle concentrations or the changes in particle concentration are much more rapid than in a boreal forest, for examples in an urban measurement location, they will have to be adjusted. Also, the composition of smallest particles might affect the ideal level of supersaturation to activate most of them without too much disturbance from homogenous nucleation.



Figure 2: Box plots of the measured 1.15 - 1.73 nm particle concentration at SMEAR II grouped with the PSM background concentration. The red line is the median concentration<u>concentration</u>, and the blue box contains 50% (25th to 75th percentile) of all data points. The whiskers mark the location of the 95th and 5th percentile data points<u>and the red plusses are outliers beyond</u> those percentiles. The number in parenthesis indicates the fraction of all data points in each bin.

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2.2.3 Measurement uncertainties

Measuring sub-3nm particles involves notable uncertainties, as small particles are very difficult to detect. Both PSM calibration and measurement are sensitive to the chemical composition of the particles being measured. The activation probability with DEG seems to be lower for organic particles than for inorganic particles. The cutoff size, the diameter at which 50% of the particles are activated in the PSM, can be over a nanometer larger for organic particles than for inorganic particles (Kangasluoma et al., 2014, Kangasluoma et al., 2016b), but there is no systematic studies for different kinds of ambient particles. Because we do not know the exact chemical composition of the particles in the ambient air, the sizing in the measurement contains uncertainties. In addition, the activation probability of particles is also slightly different for charged and non-charged (neutral) particles (Kangasluoma et al., 2016b). Due to the uncertainties, we chose to compare two rather wide size ranges, 1.1-1.7 and 1.7-2.5 nm, although the PSM data would allow also more detailed sizing.

The PSM is calibrated by measuring particles from a known source. A certain particle size is selected with a differential mobility analyzer (DMA) and an electrometer is used as a reference instrument. This gives us the PSM detection efficiency for each selected size. The PSMs in this study were calibrated using charged tungsten oxide particles in the size range between 1.0 and 3.2 nm in mobility diameter, as there is no good calibration method and reference instrument readily available for neutral particles. Therefore, the diameters given should be taken as activation-equivalent sizes (we assume that the particles would activate as charged tungsten oxide particles do). The PSM may also be sensitive to ambient conditions, mainly relative humidity (Kangasluoma et al, 2013; Jiang et al., 2011). More discussion on the uncertainties can be found in

240 Kangasluoma et al. (2020) and references therein.

When dealing with long time series, an additional complication arises from changing and maintaining equipment. While the different PSMs used in the study over the years are essentially similar devices, they have slightly varying cutoff limits and detection efficiency curves, which has been taken into account during data processing, but which could still affect the final inverted concentrations. The data preprocessing and inversion method can also produce additional uncertainties which are

difficult to quantify (Lehtipalo et al., 2014; Cai et al., 2019).

To estimate the magnitude of error<u>in the concentrations</u> caused by the uncertainties related to PSM measurement, we compared the ion concentrations detected by the PSM to those from a Neutral Cluster and Air Ion Spectrometer (NAIS,

- 250 described briefly in section 2.4), which is the only other instruments measuring in the same size range at SMEAR II. The ion concentrations were acquired from a PSM with an ion trap inlet (Wagner et al., 2017, Kangasluoma et al., 2016a) measuring in the same container as the long-term measurement PSM. The neutral PSM data was measured between April 2017 and April 2019. The setup is otherwise similar to the PSM used in the rest of this study, but the ion trap is switched on every 8 minutes and then off again after 8 minutes. This allows us to differentiate between neutral particle and total particle
- 255 concentrations and acquire the ambient ion concentration from the PSM.

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The comparison shows that the PSM detects small ions and charged particles fairly well and the overall concentrations measured with the PSM and the NAIS are of the same magnitude in the size range used in this study (Figure 3). The relative concentration (from binned y-directional medians) measured by the PSM is between 29 and 100 %, with the median relative concentration being 65 %. This suggests that most, but not all of the ambient ions are activated by the PSM, and

- that we are more likely underestimating than overestimating the ambient concentrations of small particles. It should be noted that the ions are a mixture of different chemical compounds, and the ion composition varies diurnally and seasonally in boreal forest (Ehn et al. 2010), so we expect that their activation fraction (relative to tungsten oxide ions used for calibrating the PSM), varies as well. Detailed analysis of the activation of different types of ambient ions in the PSM is subject to future
 - studies. Based on laboratory experiments which conclude that the effect of charge on the cutoff size is between 0 and 0.50 nm (Kangasluoma et al., 2016b), the above results mean that we likely activate neutral particles as well, but their activation efficiency is difficult to quantify.



NAIS 1.1 - 2.5 nm ion concentration (cm⁻³)

Figure 3: Comparison of 1.1 – 2.5 nm ambient ions measured by PSM and NAIS at SMEAR II. The orange line is the 1:1 line, the 270 blue data points are hourly medians and the red points are lognormally binned y-directional medians with the red whiskers showing the 75th and 25th percentile.

2.3 CI-APi-ToF

- We used Chemical Ionization Atmospheric Pressure interface Time of Flight Mass Spectrometer (CI-APi-TOF, Jokinen et al., 2012) with nitrate ion as a reagent ion to measure low-volatility vapors at the SMEAR II station. The detection of CI-APi-TOF is based on proton transfer reactions or clustering with the nitrate ion through collisions with nitrate ions (NO₃-), nitrate ion-nitric acid dimers (HNO₃NO₃⁻) and nitrate ion-nitric acid trimers ((HNO₃)₂NO₃⁻). The nitrate ion chemical ionization is a very selective method as nitrate ions react only with strong acids, such as malonic acid, sulfuric acid and
- 280 methane sulfonic acid (Eisele and Tanner, 1993) and oxidized organic compounds that have at least two hydroperoxy (OOH) groups or other H-bond-donating groups (Hyttinen et al., 2015). In the chemical ionization inlet ~20 liters per minute (lpm) of sheath flow is mixed with ~5 milliliters per minute flow of air saturated with nitric acid (HNO₃) and then guided to the ionization source. In the ionization source, nitric acid is ionized with

a soft x-ray source (Hamamatsu). The sheath flow with nitrate ions is guided to the drift tube where it gets mixed with the sample flow (10 lpm). The nitrate ions (or ion-clusters) and the molecules of the sample have around 200 ms of time to react

- sample flow (10 lpm). The nitrate ions (or ion-clusters) and the molecules of the sample have around 200 ms of time to react with each other in drift tube before they enter the APi of the mass spectrometer through a 0.3 mm critical orifice with flow of ~0.8 lpm. In the APi the molecules of the sample are gradually pumped out while the ions are kept in the middle of the stream by quadrupoles and ion lenses (Junninen et al 2010). In the TOF the ions are accelerated with an energy pulse and they are separated by their time of flight to reach the detector in the chamber.
- 290 The CI-APi-TOF measurements were conducted at a 35-meter altitude in a tower right next to in the same area as the ground level particle measurements. The measurement height is above the forest canopy. Zha et al. (2018) found that the HOM concentrations above and inside the canopy are similar when the boundary layer is well-mixed. The concentrations between these altitudes may differ during a strong temperature inversion or a shallow surface layer in nighttime.
- All the low-volatility vapor measurements were performed with the same instrument that was calibrated twice during this 295 measurement period with sulfuric acid calibrator (Kürten et al., 2012). In the calibrations we achieved calibration coefficients 2.4e9 cm⁻³ for 2014-2018 and 4.6e9 cm⁻³ for 2019 onwards and used the same coefficient for all detected compounds. This assumption is valid for compounds that cluster with nitrate ions at the collision limit and have equal collision rates. The collision rates of nitrate ions with SA and with HOMs are approximated to be very similar (Ehn et al., 2014). Mass spectra obtained from the instrument were analyzed using the "tofTools" program described in
- 300 Junninen et al. (2010) and unit mass resolution was used in peak integration. The uncertainty of the concentrations is estimated to be -50%/+100%.

2.4 Complementary data

The NAIS measures the mobility distribution of ions in the atmosphere between 0.8 and 40 nm and it can be used to measure either naturally charged ions or the particles can be charged with a corona discharge to measure total particle concentration (Kulmala et al., 2007). We used an automatic atmospheric NPF event classification algorithm developed by Dada et al. (2018) to determine NPF event times during the investigated time span. The event classification algorithm provided the start, peak and end times of NPF events using data from the NAIS. Relative humidity data <u>iswas-used</u> from the Rotronic MP102H RH sensor in the measurement mast at the SMEAR II station, measured at 16 (before 2/2017) and 35-meter heights. The global radiation data was measured at the same measurement mast, with the Middleton SK08 pyranometer at 18-meter height (before 9/2019) and with the EQ09 pyranometer at 35-meter height.

2.5 Analysis methods for comparing PSM and CI-APi-TOF data

We used the time series of quality controlled and inverted sub-3nm particle concentrations to study the diurnal and seasonal patterns of sub-3nm aerosol particles. The same seasonal analysis was performed on the available CI-APi-ToF data.

- 315 Measured Then, measured sub-3nm particle concentrations were then compared to the vapor concentrations to determine correlations between observed particle and vapor concentrations during NPF events. In order to ignore the effect of the diurnal cycles on the analysis, only events that occurred between 10:00 and 14:00 were included in the correlation analysis. Correlations were also separately investigated for spring- and summer- and autumntime NPF events. There were not enough data points for events during autumn and winter for separate analysis during those seasons.
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We compared the particle concentrations with measured SA and HOM concentrations since they have been identified to directly participate in NPF in laboratory studies (Sipilä et al., 2010; Kirkby et al., 2016). The HOM molecules were further divided to monomers and dimers, as well as nitrates and non-nitrates according to their elemental composition. The molecules were divided into nitrates and non-nitrates because nitrate HOMsmolecules typically have a higher volatility than non-nitrate molecules (Yan et al., 2020) and it is possible that their contribution to NPF is different (Lehtipalo et al. 2018). For each category, we summed up the concentrations of the selected peaks. For our purpose, it is not necessary to identify all possible peaks in each category, but to obtain the temporal variation of different types of particle precursors.

- For SA, HOM non-nitrate monomers and HOM nitrate monomers, we chose mass peaks 97 Th (HSO₄⁻), 340 Th 330 $(C_{10}H_{14}O_9(NO_3-))$ and 339 Th $(C_{10}H_{15}O_8N_2(NO_3-))$, respectively (Sarnela et al., 2018; Kulmala et al., 2013). In order to increase the signal-to-noise ratio, we also chose extra mass peaks based on correlation and added up their signal. For SA, we chose all mass peaks for which the logarithmic correlation coefficient with the SA monomer was higher than 0.95, and for the organic molecules we chose mass peaks for which the logarithmic correlation with the original peak was higher than 0.85. Some of the selected peaks can contain several compounds including HOM nitrate monomers and radicals. For HOM
- 335 dimers, we chose known peaks from previous studies because there was not one dominant peak to choose. For HOM nonnitrate dimers we selected 480 ($C_{18}H_{26}O_{11}$ (NO₃⁻)), 494 ($C_{19}H_{28}O_{11}$ (NO₃⁻)), 510 ($C_{20}H_{32}O_{11}$ (NO₃⁻)), 542 ($C_{20}H_{32}O_{13}$ (NO₃⁻)), 556 ($C_{20}H_{30}O_{14}$ (NO₃⁻)), 574 ($C_{20}H_{32}O_{15}$ (NO₃⁻)), 588 ($C_{20}H_{30}O_{16}$ (NO₃⁻)) and 620 Th ($C_{20}H_{30}O_{18}$ (NO₃⁻)) based on Sarnela et al. (2018). For HOM nitrate dimers we selected 538 ($C_{20}H_{32}O_{11}N_2(NO_3^{-1})$), 555 ($C_{20}H_{31}O_{13}N(NO_3^{-1})$), 570 ($C_{20}H_{32}O_{13}N_2(NO_3^{-1})$))), 586 ($C_{20}H_{32}O_{14}N_2(NO_3-)$) and 602 Th ($C_{20}H_{32}O_{15}N_2(NO_3-)$) from known peaks (Zha et al., 2018). The complete list of 340 peaks used in our analysis and their molecular formulas is listed in Table 12.

Sub-3nm particle concentrations were also compared to combinations of different precursor molecule concentrations since particle formation might involve several different vapor species. Laboratory experiments replicating boundary layer NPF in forested regions (Riccobono et al., 2014; Lehtipalo et al., 2018) and previous analysis of field data sets (Paasonen et al.,

345 2010) have shown that particle formation rates can be parametrized using a product of sulfuric acid concentration and organics concentrations. WTherefore, we expect that sulfuric acid and HOMs or some combination of them should correlate well with new particle formation in a boreal forest and the correlations in different size ranges might reveal which precursors are most important at different stages of the process.

Table <u>1</u>²: The mass peaks selected for analysis and their molecular formulas. Sulfuric acid and HOM monomer peaks were selected based on correlation with the bolded mass peaks and summed together in order to increase the signalto-noise ratio. HOM nitrate monomer peaks listed as "Several compounds" contain HOM nitrate monomers and radicals, but a single peak cannot necessarily be identified as the main compound.

	Sulfuric Acid	HOM Non-nitrate Dimers					
97 Th	HSO ₄ -	480 Th	C ₁₈ H ₂₆ O ₁₁ (NO ₃ ⁻)				
160 Th	$H_2SO_4(NO_3^-)$	494 Th	$C_{19}H_{28}O_{11}$ (NO ₃ ⁻)				
195 Th	$H_2SO_4 \cdot HSO_4^-$	510 Th	$C_{20}H_{32}O_{11}$ (NO ₃ ⁻)				
	HOM Non-nitrate Monomers	542 Th	C ₂₀ H ₃₂ O ₁₃ (NO ₃ ⁻)				
298 Th	C ₈ H ₁₂ O ₈ (NO ₃ -)	556 Th	$C_{20}H_{30}O_{14}~(NO_{3})$				
308 Th	$C_{10}H_{14}O_7(NO_3^-)$	574 Th	$C_{20}H_{32}O_{15}$ (NO ₃ ⁻)				
310 Th $C_{10}H_{16}O_8(NO_3^-)$		588 Th	$C_{20}H_{30}O_{16}~(NO_{3})$				
340 Th	$C_{10}H_{14}O_9(NO3^{-})$	620 Th	$C_{20}H_{30}O_{18}$ (NO ₃ ⁻)				
	HOM Nitrate Monomers		HOM Nitrate Dimers				
297 Th	Several compounds	538 Th	$C_{20}H_{32}O_{11}N_2(NO_3^-)$				
311 Th	Several compounds	555 Th	$C_{20}H_{31}O_{13}N(NO_3^-)$				
327 Th	Several compounds	570 Th	$C_{20}H_{32}O_{13}N_2(NO_3^-)$				
339 Th	$C_{10}H_{15}O_8N_2(NO_3^-)$	586 Th	$C_{20}H_{32}O_{14}N_2(NO_3^-)$				
		602 Th	$C_{20}H_{32}O_{15}N_2(NO_3^-)$				

355 **3 Results**

In the following section we present the 74-month time series of sub-3nm particle concentrations and the 31-month time series of aerosol precursor vapors measured at the SMEAR II –station in Hyytiälä, southern Finland and their comparison for the overlapping time period.

3.1 Time series of particle concentrations

360 The entire time series of the particle concentrations are shown in Fig. 4 and their annual variations are shown in Fig. 5. The concentrations show a clear seasonal pattern for all threeboth size bins: 1.1-1.73 nm and, 1.3 1.7 nm and 1.77-2.5 nm. We observe highest concentrations of two annual maximums for the 1.1 - 1.7 nm particles in late spring and summer (maxima in May and July), one in May and another one in July, while 1.7 - 2.5 nm particles have a clear annual maximum during earlylate spring (March) and early summer. Wand we also observe the lowest concentrations for both size classes during the

365 winter months, consistent with earlier observations at the same site (Kontkanen et al., 2017). The end of year 2016 and early 2017 show lower total concentrations than the rest of the time series. This could be due to atypical environmental conditions, but we cannot exclude technical reasons leading to diminished detection efficiency (the instrument was thereafter exchanged in spring 2017). Excluding this part of the data did





Figure 4: The monthly variation of the particle concentration in the <u>threetwo</u> PSM size bins. The red line shows the median concentration for each month and the blue box contains 50% (25th to 75th percentile) of all data points. The whiskers mark the location of the 95th and 5th percentile data points and the red plusses are outliers beyond those percentiles. The areas with the green background are spring months, the yellow background represents summer months, the brown background represents autumn months and the blue background represents winter months. <u>The tick marks visible are in the middle of each month</u>.



Figure 5: The annual variation of the particle concentration in the two PSM size bins. The red line shows the median concentration for each month and the blue box contains 50% (25th to 75th percentile) of all data points. The whiskers mark the location of the 95th and 5th percentile data points.





Figure 65: The median diurnal cycles of the particle concentrations for the <u>entire dataset (left panel)</u>, new particle formation event days (middle panel) and non-event days (right panel).11 - 1.7 nm (left panel) and 1.7 - 2.5 nm (right panel) size <u>rangesconcentrations</u>. The blue, red, and yellow lines show the concentrations for size ranges of 1.1-1.3 nm, 1.3-1.7 nm, and 1.7-2.5 nm the entire dataset, new particle formation events and non-event days, respectively. The number of days included in the median day is presented by the N at the top left of each figure. The light green, light red and lilac shading <u>areis</u> the diurnal cycles of global radiation for all data, NPF event-days and non-event days, respectively (right y-axis)(right y-axis). The number of days included in the median day is presented by the number in parenthesis in the legend.

The diurnal patterns of particle concentrations in three size bins are shown in Fig. <u>65</u>. For the entire dataset,- wWe observe two maxima_a maximum for the 1.1–1.<u>7</u>³ nm concentration in the evening and a second smaller peak in the afternoon. <u>-n</u>: one around midday and another during the evening. In this size bin, the measured concentrations can consist of both very small particles, large gas molecules <u>and/</u>or molecular clusters (Ehn et al., 2014); the distinction between them cannot be made based on the measurement. Consequently, the_<u>-daytime</u>-maximum can result from a combined effect of the diurnal behaviors of large organic molecules and newly formed molecular clusters. The diurnal variation of organic compounds is discussed below.<u>_Similarly, tT</u>he evening-time maximum can be due to organic molecular clusters, which have been observed to form during evening time by biogenic ion-induced mechanism (Rose et al., 2018). Both 1.3–1.7 nm and The 1.<u>7</u>–2.5 nm particle concentrations exhibits a daytime maximum in the afternoon_around the same time as the smaller size range, but the evening time maximum is missing in this size range. However, we observe a second, larger maximum for the <u>1.7</u>–2.5 nm particle concentration in the evening as well.

415 During regional NPF events, we expect the sub-3nm size distribution to behave differently than when there is no event, in the case that the formation of small particles takes place at our measurement location. In Fig. <u>65</u>, we <u>also</u> present diurnal cycles for NPF event and non-event days separately. Even though the event classification algorithm gives us exact event times, we used



Figure <u>76</u>: The median diurnal cycles of the particle concentrations in different seasons. <u>The left panel shows the 1.1 - 1.7 nm</u> particle concentration seasonal diurnal cycles and the right panels shows the 1.7 - 2.5 nm particle concentration seasonal cycles. At the top left is the diurnal cycle for spring, top right is for summer, bottom left for autumn and bottom right for winter. <u>The blue</u>,

- 425 red, yellow and purple lines show the seasonal diurnal cycles spring, summer, autumn and winter, respectively. The area plots in the background present the seasonal diurnal cycle for each season. The light green, light yellow, lilac and dark green shading represent spring, summer, autumn and winter, respectively. The yellow, red, and blue lines show the concentrations for the size ranges of 1.15-1.3 nm, 1.3-1.7 nm, and 1.7-2.5 nm, respectively. The number of days included in the median day is presented by the N at the bottom right of each figure. The light green shading is the diurnal cycle of global radiation (right y-axis). The number of
- 430 days included in the median day is presented by the number in parenthesis in the legend.

entire event days in this part of the analysis. The most noticeable difference between NPF event and non-event days is the strong midday maximum for both 1.31-1.77 nm and 1.77-2.5 nm particle concentrations on NPF event days. This maximum does not appear during non-event days, leading to the conclusion that the increase in midday concentrations can be attributed
to regional NPF. This is also supported by the 1.7-2.5 nm concentrations starting to rise later than the 1.1-1.7 nm concentration, consistent with the fact that it takes a while to grow the particles into the larger size range. –The concentrations are also generally higher during NPF than non-NPF days, indicating that conditions are favorable for cluster/particle formation. However, the smallest size bin 1.1-1.7 nm particle concentration does not show a clear differenceonly shows a 40 % relative increase during NPF in comparison toand non-NPF days, while the 1.7 - 2.5 nm
particle concentration increases by over 250 %.⁷ This suggests that the 1.7 - 2.5 nm particle concentration is more directly related to new particle formation. ItThis maycould also mean that the production and sinks of 1.1–1.7 nm3 particles are large enough that the enhanced growth into the 1.7<u>3</u>-<u>2.5</u>1.7 nm particle size range during event times is not visible in the concentration not the largest contributing factor in the concentration.

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Because the formation mechanism and thus particle concentrations can vary depending on the season, we studied the diurnal cycles-of each particle concentration size class separately for each season (Figure <u>76</u>). We observe the largest concentrations of 1.1-1.7 nm particles during summer and the lowest during winter which is likely connected due to the biogenic activity in the surrounding forest. During spring and summer <u>Tthe-particle</u>-concentrations of 1.1-1.7 nm particles have distinct

450 maximaums in the early afternoon and also in the evening. during spring and summer and additionally, there is a daytime maximum in the early afternoon during summer. These evening peaks have been linked to the formation of large organic clusters (Rose et al., 2018). Thus, it is not surprising that they are absent in the autumn-winter data. However, autumn and winter concentrations have a single maximum in the late afternoon. These late afternoon and evening peaks all occur several hours after global radiation has gone down to essentially zero, indicating that the formation mechanism does not require sunlight. However, it should be kept in mind that also the boundary layer dynamics can affect the measured concentrations.

These evening peaks in concentration have been linked to the formation of organic clusters (Rose et al., 2018), while the lack of clear daytime maximum suggests that 1.1–1.7 nm particles are not very strongly connected to NPF.

- The larger size bin of 1.7 2.5 nm particles exhibits the largest median concentrations during spring and summer, but the diurnal variation is rather similar in all seasons. The higherincreased concentration during spring, which has a slightly higher median concentration than even summer, can be at least partially attributed to an increased frequency of regional NPF (Nieminen et al., 2014). Additionally, we observe clear early afternoon maximaums during spring, summer and autumn that can likely be linked to new particle formation, while the concentrations during nighttime are very low. Concentrations during winter have a weaker diurnal cycle and lower median concentration, consistent with observations that NPF is rare during winter time.
- 465 <u>wintertime.</u>

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(Dada et al., 2017; Nieminen et al., 2014)

During springtime, the diurnal pattern of 1.1 1.3 nm concentration has two maxima, a daytime, and an evening maximum.
 We observe up to three times larger concentration of 1.3 1.7 nm particles during spring compared to the average diurnal concentrations for other seasons. This increase in particle concentration likely results from the increased frequency of regional NPF during spring (Nieminen et al., 2014).

During the summer, we observe the highest 1.1 1.3 nm particle concentrations out of all seasons. This is likely due to the
increased biogenic activity in the surrounding forest and stronger photochemical production of precursor vapors. The diurnal pattern of the 1.1 1.3 nm concentration exhibits the same two maxima as the diurnal pattern of the entire dataset. However, the 1.3 1.7 nm particle concentration does not show a clear diurnal pattern, and the 1.7 2.5 nm concentration only exhibits a weak early morning maximum and a minimum between 16:00 and 17:00. This lack of diurnal pattern and the low concentration of 1.3 1.7 nm and 1.7 2.5 nm particle concentration is likely linked to a decreased frequency of NPF during summer (Dada et al., 2017).

In autumn, the 1.1–1.3 nm particle concentration has a weak but otherwise similar diurnal pattern to summer and springtime concentrations. We observe no discernable diurnal pattern for the 1.3–1.7 particle concentration. The 1.7–2.5 nm particle concentration has a weak diurnal pattern, but the overall concentration is notably lower than in summer and spring, particularly during night time.

During the winter, we observe the lowest median concentrations of 1.1–1.3 nm particle concentrations. Additionally, the concentrations of 1.1–1.3 nm, 1.3–1.7 nm and 1.7–2.5 nm particle concentrations exhibit only a single, small midday maximum. This supports the idea that the evening maximum is related to the formation of organic clusters (Rose et al.,

490 2018). The fact that sub-3nm particle concentrations during winter are generally low is consistent with earlier observations that NPF is rare during wintertime (Dada et al. 2017; Nieminen et al. 2014).

3.2 Time series of vapor concentrations

The time series of the precursor vapors are shown in Fig. <u>87 and theirits annual variation is presented in Fig. 9.</u> We observe the highest concentrations of all studied vapors <u>during summerbetween late spring and early autumn-months</u> and the lowest concentrations in either late autumn, winter, or early spring. <u>This can be explained by the annual behaviour of the precursors</u> of the studied vapors. The main pathway for sulphuric acid formation is oxidation of SO₂ by OH, and formation of OH is strongly dependent on radiation, whereas the monoterpene emissions are strongly dependent on the temperature (Guenther et al. 1995) and thus are highest from late spring and to early autumn (Rantala et al. 2015; Hakola et al. 2003). There are no visible differences in concentrations between different years, but there are more outliers in the vapor concentrations during 2014 and 2015.





Figure 87: The time series of the selected atmospheric aerosol precursor vapors. From the top down, the time series are shown for sulfuric acid, HOM non-nitrate monomer, HOM non-nitrate dimer, HOM nitrate monomer and HOM nitrate dimer concentrations, respectively. The time series are from April 2014 to April 2020. The red line is the median concentration for each month and the blue box contains 75% of all data points. The whiskers mark the location of the 95th and 5th percentile data points and the red plusses are outliers beyond those percentiles. The areas with the green background are spring months, the yellow background represents summer months, the brown background represents autumn months and the blue background represents winter months.



Figure 9: The annual variation of the analyzed precursor vapors. The red line shows the median concentration for each month and the blue box contains 50% (25th to 75th percentile) of all data points. The whiskers mark the location of the 95th and 5th percentile

515 data points.

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We also analyzed the diurnal behavior of the measured aerosol precursor vapors in the same fashion as the particle concentrations discussed above. The diurnal patterns of SA, HOM monomer (nitrate and non-nitrate) and HOM dimer (nitrate and non-nitrate) concentrations for the entire dataset are shown in Fig. <u>108</u>. SA concentration has a similar diurnal pattern to that of global radiation, which is expected as sulfuric acid is formed in the atmosphere mainly through photochemical oxidation (Lucas and Prinn, 2005; Petäjä et al., 2009). HOM non-nitrate monomer concentration has a minimum in the early morning, with the concentration rising throughout the day until the maximum is reached after 18:00. In



Figure 9: The diurnal cycles of precursor vapors in different seasons. At the top left there is the diurnal cycle in spring, at the top 525 right there is the diurnal cycle in summer, at the bottom left there is the diurnal cycle in autumn and at the bottom right there is the diurnal cycle in winter. The blue line is the sulfuric acid concentration, red line is the HOM non-nitrate monomer concentration, the yellow line is the HOM nitrate monomer concentration. The yellow line is the HOM non-nitrate dimer econcentration and the green line is the HOM nitrate dimer concentration. The number of days included in the median day is presented by the N in each figure. The light green shading is the diurnal cycle of global radiation (right y-axis).



<u>concentration, red_line_is_the_HOM_non-nitrate_monomer_concentration, the_purple_line_is_the_HOM_nitrate_monomer</u>
 <u>concentration, the_vellow_line_is_the_HOM_non-nitrate_dimer_concentration, and the_green_line_is_the_HOM_nitrate_dimer</u>
 <u>concentration.</u> The number of days included in the median day is presented by N at the top right of each figure. The light green, light red and lilac shading are the diurnal cycles of global radiation for all data, NPF event-days and non-event days, respectively (right y-axis).

- 540 contrast, HOM nitrate monomer concentration exhibits a single daytime peak around midday similar to the sulfuric acid concentration, but a slower decrease towards the night following the diurnal behaviour of NO in the atmosphere (Yan et al 2016, ACP). HOM dimer (both nitrate and non-nitrate) concentrations have different diurnal cycles than the other vapors, exhibiting minima during daytime and an increased concentration at night. Similar patterns were During night-time the termination reactions of RO₂ radicals with NO and HO₂ are less likely and, thus, termination reaction with another RO₂
- 545 <u>radical, resulting to dimer formation, is more plausible. Similar patterns have been</u> found by Bianchi et al. (2017) using CI-APi-ToF data from spring 2013 in Hyytiälä and Jokinen et al. (2017) during a solar eclipse.

During regional NPF event days, the concentrations of all analyzed aerosol precursor vapors are higher than during nonevent days (Figure <u>108</u>). However, the diurnal patterns of the precursor vapors are otherwise <u>rather</u> similar on event and non-

- 550 event days. <u>The non-nitrate monomers and dimers show a small increase during daytime on NPF days which is absent on</u> <u>non-event days.</u> Additionally, we observe that the aerosol precursor vapor concentrations rise earlier and the difference in concentrations between the night-time and the daytime is larger on NPF event days. These observations, together with the <u>diurnal patterns of global radiation in Figures 6 and 9</u>, suggest that during event days there is more photochemical production and potentially also higher emissions of biogenic vapors. <u>This is further corroborated by the diurnal patterns of global</u>
- 555 radiation in Figures <u>65 and <u>98</u>. However, from the diurnal variations is not possible point out a single vapor explaining the difference between NPF events and non-events.</u>

The diurnal behavior of SA has a similar daytime maximum as the 1.1 1.73 nm particle concentration <u>during NPF event</u> days. when we compare the diurnal behaviors of the entire particle and vapor concentration data sets. Additionally, the diurnal behavior of sulfuric acid matches that of the 1.7 2.5 3 1.7 nm and 1.7 2.5 nm particle concentrations during event days as well. This points to the importance of suggests that sulfuric acid plays a role in atmospheric cluster formation and in the initial stages of aerosol growth. The HOM non nitrate monomer and dimer as well as HOM nitrate dimer maximum in the evening coincides with the observed peak in 1.1 1.73 nm particle concentration, meaning implying that this maximum can is belikely due to formation of organic clusters.

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In Fig. <u>119</u>, we show the diurnal patterns of precursor vapor concentrations separately for each season. <u>Sulfuric acid exhibits</u> the largest overall peak concentrations during spring, when we have the highest frequency of NPF events (Nieminen et al., 2014). All organic vapors we analyzed exhibited the highest median concentrations during summer and the lowest median concentrations during winter, which can be explained by the seasonality of solar radiation and VOC emissions (Hellén et al., 2018).

Sulfuric acid follows the diurnal behaviour of solar radiation in each season fairly well, as expected. HOM non-nitrate monomers and dimers both have an evening peak and the time of the maximum shifts seasonally. HOM nitrate monomers have a daytime maximum while HOM nitrate dimers have a daytime minimum during all seasons but summer. During

575 <u>summer, both HOM nitrate and non-nitrate dimers have a small midday maximum with two minima, one in the morning and</u> <u>one in the evening. The seasonal changes in the HOM diurnal cycles result from the seasonality in solar radiation, emissions</u> <u>and boundary layer dynamics. are likely based on the seasonality of solar radiation's and temperature's diurnal behavior.</u> 580 During spring, the diurnal patterns of all studied vapors exhibit similar behavior when compared to the diurnal behavior in the entire dataset. This underlines the effect of spring and summertime data on the entire dataset because the diurnal cycles during these seasons are fairly similar and will therefore dominate the dataset.

In summer, the diurnal behaviors of sulfuric acid and HOM dimer concentrations are fairly similar to springtime behavior.
 The HOM monomer concentration does not rise as strongly during the day as during spring, but we still observe a sharp increase in HOM non nitrate monomer concentration during the evening. Also, in summertime HOM nitrate monomer concentration reaches a maximum earlier than in spring, around 9:00 This is most likely because there is solar radiation available for a longer period of time during summer. Overall, the HOM monomer concentrations are as much as five times higher during the summer than during spring and the concentrations of other HOMs are higher as well. The observed high
 HOM concentrations during summer can be explained by high emissions of organic vapors from the surrounding forest

(Hellén et al., 2018) and increased photochemical activity.

In autumn, sulfuric acid concentration shows a daytime maximum around midday, but the concentration rises later in the morning and decreases earlier in the afternoon than during spring and summer. Additionally, the daytime sulfuric acid peak
 is smaller. Similarly, HOM monomer concentrations begin to rise later during the morning than in spring or summer, most likely because of the seasonality of solar radiation's diurnal behavior. Overall, the median concentrations and diurnal behaviors during autumn are comparable to springtime diurnal behaviors of the vapors, with the exception that the concentration of HOM nitrate monomers is lower and more comparable to winter concentrations. HOM dimer diurnal behaviors are similar to spring, but nighttime concentrations are higher and the period of decreased concentrations during the seasonal differences in global radiation.



Figure 8: The diurnal cycle for each selected atmospheric precursor vapor for the entire dataset (left panel), for new particle formation event days (middle panel) and for non-event days (right panel). The blue line is the sulfuric acid concentration, red line is the HOM non-nitrate monomer concentration, the purple line is the HOM nitrate monomer concentration, the yellow line is the HOM non-nitrate dimer concentration and the green line is the HOM nitrate dimer concentration. The number of days included in the median day is presented by N at the top right of each figure. The light green shading is the diurnal cycle of global radiation (right y-axis).



- 610 Figure 11: The diurnal cycles of precursor vapors in different seasons. At the top left is the diurnal cycle in spring, at the top right the diurnal cycle in summer, at the bottom left the diurnal cycle in autumn and at the bottom right the diurnal cycle in winter. The blue line is the sulfuric acid concentration, red line is the HOM non-nitrate monomer concentration, the yellow line is the HOM non-nitrate dimer concentration and the green line is the HOM nitrate dimer concentration. The number of days included in the median day is presented by the N in each figure. The light green shading 615 is the diurnal cycle of global radiation (right v- axis). The light green, light vellow, lilac, and dark green shading represent spring, summer, autumn and winter, respectively.
- In winter, the concentrations of precursor vapors are lower than during other seasons and their diurnal variation is smaller. 620 Sulfuric acid and HOM monomer concentrations begin to rise later in the morning, around 09:00-10:00, again likely due to the seasonality of solar radiation diurnal behavior. HOM nitrate dimer concentration behavior remains similar to other seasons, but the median concentration is lower. Notably, the HOM non-nitrate dimer concentration has a barely detectable diurnal cycle during the winter.

625 <u>Table 2: The descriptive statistics of both particle and vapor concentrations used in the data both for the entire dataset and for</u> each season separately. The median values are bolded with the 25th and 75th percentiles included in parenthesis.

Concentration (cm ⁻³)	Median	Median Spring	Median	Median	Median	
	<u>concentration</u>	<u>concentration</u>	<u>Summer</u>	<u>Autumn</u>	<u>Winter</u>	
	<u>(25th-75th)</u>	<u>(25th-75th)</u>	<u>concentration</u>	<u>concentration</u>	<u>concentration</u>	
			<u>(25th-75th)</u>	<u>(25th-75th)</u>	<u>(25th-75th)</u>	
<u>1.1–1.7 nm particles</u>	<u>163 (88–289)</u>	206 (116–395)	<u>281 (181–445)</u>	<u>144 (78–222)</u>	84 (45–137)	
<u>1.7–2.5 nm particles</u>	<u>8 (3–19)</u>	<u>12 (5–31)</u>	<u>9 (4–21)</u>	<u>6 (2–16)</u>	<u>6 (2–15)</u>	
Sulfuric Acid	<u>2.97e+05</u>	<u>5.26e+05</u>	<u>5.53e+05</u>	<u>1.57e+05</u>	<u>8.86e+04</u>	
	<u>(9.33e+04 –</u>	<u>(1.72e+05 –</u>	<u>(2.51e+05 –</u>	<u>(5.76e+04 –</u>	<u>(4.43e+04 –</u>	
	<u>9.65e+05)</u>	<u>1.14e+06)</u>	<u>1.28e+06)</u>	<u>4.97e+05)</u>	<u>1.78e+05)</u>	
HOM non-nitrate	<u>1.63e+06</u>	<u>2.08e+06</u>	<u>4.49e+06</u>	<u>8.89e+05</u>	<u>4.31e+05</u>	
monomers	<u>(4.87e+05 –</u>	<u>(7.13e+05 –</u>	<u>(2.68e+06 –</u>	<u>(3.07e+05</u> –	<u>(1.40e+05 –</u>	
	<u>4.32e+06)</u>	<u>4.82e+06)</u>	<u>8.44e+06)</u>	<u>2.49e+06)</u>	<u>1.11e+06)</u>	
HOM non-nitrate	<u>2.36e+05</u>	<u>2.42e+05</u>	<u>6.17e+05</u>	<u>2.11e+05</u>	<u>8.83e+04</u>	
<u>dimers</u>	<u>(1.02e+05 –</u>	<u>(1.01e+05 –</u>	<u>(3.20e+05 –</u>	<u>(1.16e+05 –</u>	<u>(4.92e+04</u> -	
	<u>5.68e+05)</u>	<u>4.84e+05)</u>	<u>1.28e+06)</u>	<u>4.63e+05)</u>	<u>1.65e+05)</u>	
HOM nitrate	<u>1.52e+06</u>	<u>2.20e+06</u>	<u>6.79e+06</u>	<u>6.38e+05</u>	<u>2.23e+05</u>	
monomers	<u>(3.22e+05 –</u>	<u>(6.33e+05 –</u>	<u>(3.40e+06 –</u>	<u>(2.31e+05</u> -	<u>(9.42e+04 –</u>	
	<u>5.68e+06)</u>	<u>6.23e+06)</u>	<u>1.20e+07)</u>	<u>2.74e+06)</u>	<u>6.61e+05)</u>	
HOM nitrate dimers	<u>1.13e+05</u>	<u>1.25e+05</u>	<u>1.50e+05</u>	<u>1.15e+05</u>	<u>4.06e+04</u>	
	<u>(4.17e+04 –</u>	<u>(7.83e+04 –</u>	<u>(7.83e+04 –</u>	<u>(4.43e+04</u> -	<u>(1.19e+04 –</u>	
	<u>3.00e+05)</u>	<u>2.98e+05)</u>	<u>3.61e+05)</u>	<u>4.57e+05)</u>	<u>1.20e+05)</u>	

630 **3.3** The connection between precursor vapors and the formation of sub-3nm particles

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We used correlation analysis to investigate the relationship between atmospheric sub 3nm-particle concentrations and the selected atmospheric vapors. <u>Here, Thethe NPF</u> data is from <u>NPF</u> event times as specified by the NPF event algorithm and only from events occurring between 10 and 14 as to diminish the effect of the diurnal cycles on the correlations. Limiting our data selection to this time range diminishes the effect of meteorological variables on our analysis and allows us to focus on daytime NPF events. Because absolute vapor concentrations are not needed for this analysis, we used the aerosol precursor

vapor data without the calculated calibration coefficients to eliminate this source of uncertainty. The results are shown in Table $\underline{32}$.

- Particle concentrations show positive correlation with all the measured precursor vapors, but we can see slight differences
 between the two size ranges and between NPF event times and the whole data set. during NPF events show clear correlations with sulfuric acid and with HOM dimer concentrations. Notably, sulfuric acid concentration correlates particularly with 1.77 2.5 nm concentrations, underlining its importance in the initial growth of the newly formed particles or determining when NPF events happen. The smallest particles correlate better with HOMs than SA, especially when looking at the whole data set, confirming that this size range is influenced by organic molecules or clusters. In the larger size range the correlations are quite similar for all vapors when looking at the whole data set, but during NPF events, the correlation with
- SA is higher than with the organic precursors. -This could indicate that SA is crucial in determining when the particles grow over the 1.7 nm threshold. HOM monomers correlate only with the smallest size bin, while HOM dimers correlate with all sub 3nm concentrations measured with the PSM, especially during event times. This indicates that HOM dimers are important in the formation of the smallest atmospheric particles, a finding consistent with Lehtipalo et al. (2018). The best
- 650 correlation is found between HOM nitrate dimer concentration and 1.3 1.7 nm particle concentrations.

The best correlations during NPF events was found between thewith 1.1 1.7 nm particle concentrations and is-with the product of SA and HOM nitrate dimers in both size classes-during events. The scatter plots for the best correlations between atmospheric vapors and sub-3nm concentrations are shown in Fig. 12. It is quite interesting that including HOM nitrate dimers improves the correlation slightly compared to just SA, even though they have a completely different diurnal variation. It is possible that both sulfuric acid and large organic molecules are required for the formation and growth of new particles, which would explain the observed correlations. However, the correlation can also point to two separate formation

pathways, organic and inorganic (Yan et al., 2018).

660 The combination of HOM (nitrate or non nitrate) dimer and sulfuric acid concentration correlates most strongly with the 1.73 21.57 nm and 1.7 2.5 nm particle concentrations. This is consistent with IL aboratory experiments in the CLOUD chamber have shown, showing that particle formation rates at 1.7 nm correlate with the product of sulfuric acid, ammonia and non-nitrate HOM dimers (Lehtipalo et al., 2018). However, we observe that HOM nitrate dimers have a better correlation with the particle concentrations than the HOM non-nitrate dimers. We would expect the opposite, as non-nitrate

665 HOMs have lower volatility than nitrate HOMs (Yan et al., 2020). This discrepancy with the laboratory results could be explained by the nitrate HOMs being better correlated with global radiation (Figure <u>108</u>), as NPF most frequently occurs at the SMEAR II station during the global radiation maximum. However, the difference in correlation coefficients is not <u>necessarily very</u> large <u>considering with the uncertainties involved</u>, so it could also mean that at least some of the nitrate dimers already have low enough volatility to participate in NPF, especially together with SA.

The scatter plots for the best correlations between atmospheric vapors and sub 3nm concentrations are shown in Fig. 120. It is possible that both sulfuric acid and large organic molecules are required for the formation and growth of new particles, which would explain the observed correlations. However, the correlation can also point to two separate formation pathways, organic and inorganic (Yan et al., 2018). HOM nitrate monomers, on the other hand, do not correlate well with sub 3nm concentrations, although

Table <u>32</u>: Logarithmic Pearson correlations between particle concentrations in different size bins measured with the PSM and known precursor vapors or combinations of precursor vapors. The data from NPF events occurring between 10 and 14 is used. Statistically significant values (p < 0.05) are bolded and values higher than 0.5 are highlighted with red color.

	1.1 1.3 nm concentration		1.3	1.3 1.7 nm concentration		1.7 2.5 nm	
			conce			entration	
	Events	All data	Events	All data	Events	All data	
Sulfuric Acid (SA)	0.27	0.37	0.37	0.3	0.57	0.37	
HOM Non nitrate Monomers	0.16	0.53	0.08	0.08	0.13	0.29	
HOM Non Nitrate Dimers	0.28	0.55	0.5 4	- 0.04	0.26	0.25	
HOM Nitrate Monomers	0.05	0.48	-0.07	0.04	0.04	0.3	
HOM Nitrate Dimers	0.53	0.49	0.62	0.12	0.52	0.33	
SA X HOM Nitrate Monomers	0.08	0.45	0.2 4	0.1 4	0.39	0.32	
HOM Non nitrate Monomers X HOM Nitrate Monomers	0.11	0.5	θ	0.06	0.09	0.3	
SA X HOM Non-nitrate Monomers	0.19	0.47	0.36	0.18	0.5	0.3 4	
SA X HOM Non-nitrate Dimers	0.33	0.52	0.62	0.18	0.61	0.4	
SA X HOM Nitrate Dimers	0.48	0.43	0.77	0.31	0.66	0.44	
SA X HOM Non-nitrate Monomers^2	0.15	0.5	0.31	0.11	0.41	0.31	
SA^2 X HOM Non-nitrate Monomers^2	0.23	0.44	0.37	0.23	0.5 4	0.35	
SA^2 X HOM Non-nitrate Dimers	0.32	0.49	0.53	0.25	0.62	0.41	
SA^2 X HOM Nitrate Dimers	0.41	0.38	0.73	0.33	0.64	0.43	
SA^2 X HOM Nitrate Monomers	0.15	0.43	0.3	0.2	0.47	0.35	
SA^2	0.27	0.37	0.37	0.3	0.57	0.37	

	<u>1.1–1.7 nm c</u>	oncentration	<u>1.7–2.5 nm concentration</u>			
	Events	<u>All data</u>	Events	<u>All data</u>		
Sulfuric Acid (SA)	<u>0.42</u>	<u>0.43</u>	<u>0.6</u>	<u>0.33</u>		
HOM Non-nitrate Monomers	<u>0.32</u>	<u>0.57</u>	<u>0.44</u>	<u>0.3</u>		
HOM Non-Nitrate Dimers	<u>0.37</u>	<u>0.58</u>	<u>0.34</u>	<u>0.24</u>		
HOM Nitrate Monomers	<u>0.23</u>	<u>0.54</u>	<u>0.43</u>	<u>0.3</u>		
HOM Nitrate Dimers	<u>0.58</u>	<u>0.51</u>	<u>0.33</u>	<u>0.19</u>		
SA X HOM Nitrate Monomers	<u>0.22</u>	<u>0.5</u>	<u>0.38</u>	<u>0.26</u>		
HOM Non-nitrate Monomers X HOM Nitrate	<u>0.26</u>	<u>0.56</u>	<u>0.42</u>	<u>0.31</u>		
Monomers						
SA X HOM Non-nitrate Monomers	<u>0.34</u>	<u>0.53</u>	<u>0.41</u>	<u>0.26</u>		
SA X HOM Non-nitrate Dimers	<u>0.46</u>	<u>0.59</u>	<u>0.48</u>	<u>0.26</u>		
SA X HOM Nitrate Dimers	<u>0.62</u>	<u>0.48</u>	<u>0.6</u>	<u>0.28</u>		
SA X HOM Non-nitrate Monomers ²	<u>0.28</u>	<u>0.54</u>	<u>0.31</u>	<u>0.23</u>		
SA^2 X HOM Non-nitrate Monomers ²	<u>0.38</u>	<u>0.5</u>	<u>0.5</u>	<u>0.29</u>		
SA^2 X HOM Non-nitrate Dimers	<u>0.47</u>	<u>0.57</u>	<u>0.57</u>	<u>0.31</u>		
SA^2 X HOM Nitrate Dimers	<u>0.56</u>	<u>0.45</u>	<u>0.63</u>	<u>0.32</u>		
SA^2 X HOM Nitrate Monomers	<u>0.29</u>	<u>0.49</u>	<u>0.47</u>	<u>0.29</u>		
<u>SA^2</u>	<u>0.42</u>	<u>0.43</u>	<u>0.6</u>	<u>0.33</u>		

they also show a daytime maximum like sulfuric acid, and in some earlier studies they have been connected to cluster formation (Jokinen et al., 2017). This supports the concept that HOM nitrate monomers have higher volatilities than other HOMs, so they might participate in later growth of particles, but not in clustering and initial growth (Yan et al., 2020; Lehtipalo et al., 2018).





690 Figure 120: The best logarithmic correlations between particle concentrations measured by PSM in <u>two</u>three size bins and precursor vapors during NPF events occurring between 10 and 14. The correlations of sub-3nm particle concentrations and sulfuric acid are on the left, the correlations of sub-3nm particle concentrations and HOM nitrate dimers are in the middle and the correlations of sub-3nm particle concentrations and the product of sulfuric acid and HOM nitrate dimers are on the right.

695 Due to the differences observed in the diurnal cycles of both sub-3nm particle concentrations and vapor concentrations between different seasons, we investigated the correlation between sub-3nm particle concentrations and atmospheric vapors separately in different seasons. Because of the lack of data for both vapor and particle concentrations during winter NPF events, we were only able to analyze spring, summer, and autumn events. The results of the seasonal NPF analysis are shown in Table <u>43</u>.

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Table <u>43</u>: Logarithmic <u>Pearson</u> correlations of known precursor vapors with particle concentrations <u>in three size bins</u> for spring (Spr.), summer (Sum.), and autumn (Aut.) seasons during event times between 10:00 and 14:00. Winter did not have enough available event points for correlation analysis. Statistically significant values (p < 0.05) are bolded and values higher than 0.5 are highlighted with red color.

		1.1–1.3 nm			1.3 1.7 nm			1.7 2.5 nm		
		concentration			concentration			concentration		
		Spr.	Sum.	Aut.	Spr.	Sum.	Aut.	Spr.	Sum.	Aut.
	Sulfuric Acid	0.15	-0.36	0.02	0.27	0.21	0.17	0.48	0.34	-0.12
	HOM Non nitrate Monomers	-0.46	0.15	0.47	0.34	-0.26	0.16	-0.21	0.69	0.44
	HOM Non nitrate Dimers	0.19	-0.58	0.57	0.87	0.42	0.18	0.29	-0.14	0.46
	HOM Nitrate Monomers	-0.51	0.12	0.4	0.18	-0.23	0.16	-0.06	0.56	0.25
	HOM Nitrate Dimers	0.61	0.31	0.5 4	0.74	-0.06	-0.04	0.45	0.13	0.64
05										
		<u>1.1–1.7 nm c</u>			oncentration <u>1</u> .		<u>1.7</u>	7–2.5 nm concentration		
			<u>Spr. Su</u>		<u>ım.</u>	<u>m. Aut.</u>		<u>or.</u>	<u>Sum.</u>	<u>Aut.</u>
	Sulfuric Acid		<u>0.34</u>	<u>0</u> .	.37	<u>0.22</u>	<u>0</u>	.4	0.26	<u>0.59</u>
	HOM Non-nitrate Monomers		<u>0.17</u>	<u>0.</u>	<u>.51</u>	<u>0.66</u>	<u>0.</u>	<u>13</u>	<u>0.59</u>	<u>0.76</u>
	HOM Non-nitrate Dimers		<u>0.25</u>	<u>0.</u>	.75	<u>0.73</u>	<u>0.</u>	<u>03</u>	<u>0.01</u>	<u>0.72</u>
	HOM Nitrate Monomers		<u>0.01</u>	<u>0.</u>	<u>.45</u>	<u>0.63</u>	<u>0.</u>	<u>06</u>	<u>0.37</u>	<u>0.79</u>
	HOM Nitrate Dimers		<u>0.68</u>	<u>-0</u>	.25	<u>0.53</u>	<u>0.</u>	<u>46</u>	<u>-0.29</u>	<u>0.3</u>

The analysis reveals clear seasonal differences between correlations of precursor vapors and sub-3nm particle concentrations. During springtime NPF events, HOM<u>nitrate</u> dimers_-correlate with <u>bothall</u> size bins of measured sub-3nm particle concentrations. This is consistent with the results of Yan et al. (2018), who compared vapor concentrations with

- 710 particle measurements performed with the NAIS. Additionally, sulfuric acid correlates <u>fairly</u> well with 1.<u>7</u>7–2.5 nm particle concentrations. <u>The springtime correlations are qualitatively similar than in the whole data set</u>, probably because majority of <u>NPF events happen in spring</u>. <u>Interestingly, HOM monomers anticorrelate with 1.1–1.3 nm and 1.7–2.5 nm particle concentrations during NPF events in spring, maybe because dimer formation is a sink of the monomers.</u>
- During summertime events, we do not observe as many statistically significant correlations. HOM monomers correlate with 715 the 1.77 - 2.5 nm particle concentrations while correlations HOM non-nitrate dimers slightly anticorrelate. with 1.71 - 21.53 nm particle concentrations. HOM monomers and Especially, the non-nitrate dimers correlate well with 1.1-1.7 nm particle concentrations, which reinforces the earlier observation that we likely measure some organic clusters in the smallest size bin. It is possible that HOM nitrate dimer anticorrelation this is caused by the higher evaporation rate of HOM dimers with the

increased temperature (Donahue et al., 2011). However, due to the lack of vapor concentration data from summer months, the amount of data available for analysis here is limited and thus correlations may not be representative.

- Also Deduring autumn, the HOM monomers and the non-nitrate dimer correlate better with the 1.1 1.73 nm particle concentrations than the nitrate dimer or sulfuric acid, a notable difference from spring. The correlation coefficients are rather high in both size ranges, perhaps the diminishing concentrations of organics make them a limiting factor for particle formation in autumn. while sulfuric correlates better with the 1.7 2.5 nm particle concentration. HOM non nitrate monomers
- also correlate with the 1.7 2.5 nm particle concentration. In addition, both HOM non nitrate dimers correlate better with 725 1.1 1.73 nm and 1.77 2.5 nm particle concentrations than during spring while the opposite is true for HOM nitrate dimers. We also do not observe statistically significant correlations with the 1.3 1.7 nm particle concentration and precursor vapors. All in all, although the correlation analysis alone cannot resolve the relative contributions of the different precursors, These differences in correlations between particle and vapor concentrations point to an annual variation in the formation
- mechanisms of sub-3nm particles. 730

It should be noted that SA do not form particles by itself at concentrations relevant to atmospheric boundary layer (Kirkby et al. 2011). Rather, it needs ammonia (NH₃) or amines to stabilize the forming clusters. It is yet unclear if SA can form stable clusters with HOMs, although SA-organics nucleation has been proposed (e.g. Riccobono et al. 2014). Lehtipalo et al.

735 (2018), showed that SA and HOMs do not to interact unless NH_3 is present. As there is no continuous ammonia and amine measurements available at SMEAR II, we could not include those in the correlation analysis, although variations in these vapors can affect the NPF mechanism and thus our results, especially the seasonal variation. Hemmilä et al. (2018) showed that there is a weak positive correlation between 1-2 nm particles measured with the PSM and ammonia and dimethylamine concentrations.

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4 Conclusions

In this study, we analyzed five years of sub-3nm particle concentration and aerosol precursor vapor concentration data from the SMEAR II station in Hyytiälä, southern Finland. The sub-3nm particle concentrations were measured with the PSM and the aerosol precursor molecule concentration data was measured with the CI-APi-ToF.

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The analysis of the PSM background counts and stability shows that to operate the PSM at the SMEAR II station in such a way that it reliably activates sub-3nm atmospheric particles, the measured background in the PSM should be within 1 and 10 cm⁻³. Too low a background, and consequently too low a supersaturation level in the PSM, results in poor activation of atmospheric sub-3nm particles. When the supersaturation is too high, the measurement becomes unstable and the observed concentrations are affected by homogenic nucleation of the working fluid. The settings of the PSM indicated by this analysis are valid for the SMEAR II station and other similar boreal background stations, but when measuring in other environments, the optimal background level may be different.

- Sub-3nm particle concentrations exhibit clear differences between NPF event and non-event days. Overall, the
 concentrations of both 1.1-1.7 nm and 1.7 2.5 nm particles are higher during NPF events and 1.7-2.5 nm particle
 concentrations exhibit a strong midday maximum during NPF event days that is not observed during non-event days. The
 size distribution of sub-3nm particles also shows a clear seasonal cycle. The 1.1-1.73 nm particle concentrations have the
 highest concentrations during the summer, which coincides with increased summertime photochemical activity and biogenic
 activity in the surrounding forest. The 1.73-2.54.7 nm and 1.7 2.5 nm particle concentrations, on the other hand,
 exhibitsshow the largest median concentrationa marked increase during springtime, coinciding with increased regional NPF
 frequency. The diurnal patterns of 1.7 2.5 nm sub 3nm concentrations exhibit clear daytime maxima around midday. Theis
 daytime maximum in concentrations is clear the clearest during spring, summer and autumn, during which regional NPF
 events are also morest common. A second maximum in the evening is observed for the 1.1-1.73 nm particles during spring
 and summer, but not for the concentrations in bigger size ranges or during wintertime. This maximum may be linked to large
- 765 organic clusters that form but do not grow to larger particles in the atmosphere.

The precursor vapors also show seasonal variability. The concentrations of all selected precursor vapors are the highest during summer and the lowest during winter. This is attributed to increased biogenic activity in the surrounding forest during the warmer periods of the year, as well as increased photochemical production. Additionally, the concentrations of sulfuric acid and HOM monomers have seasonally changing diurnal behavior because of solar radiation. All of the precursor vapor concentrations are clearly higher on NPF event days compared to non-event days and their diurnal cycle is more pronounced.

When comparing sub-3nm particle concentrations with aerosol precursor vapors, we found that the smallest particles (1.1-1.73 nm) correlate with HOMs when looking at the whole time series, indicating their presence in this size range. The 1.3-1.7 nm and 1.7-2.5 nm particles, which are more directly connected to NPF events, correlate with <u>sulfuric acid SA</u> and HOM dimers (and the product of these) during NPF events. <u>but not with HOM monomers</u>. There was no significant difference between nitrate and non-nitrate HOMs regarding their correlations with sub-3nm particles. <u>During springtime, nitrate dimers</u> seemed to correlate better than other HOMs, but the other seasons showed opposite behavior, so our conclusions regarding the role different types of HOMs remain inconclusive. The seasonal analysis of the correlations reveals some differences hetween the seasons, which could he due to change in the mechanism forming clusters. Hereway understanding the

780 between the seasons, which could be due to changes in the mechanism forming clusters. However, understanding the seasonal differences in the formation mechanisms of HOMs and sub-3nm particles in detail requires further studies.

Data availability. The meteorological data from the SMEAR II station can be accessed from the smartSMEAR website: <u>http://avaa.tdata.fi/web/smart/</u>. The data is licensed under a Creative Commons 4.0 Attribution (CC BY) license. The particle 785 concentration data measured with PSM is available at https://doi.org/10.5281/zenodo.4153280. Theand vapor concentration data measured-with PSM, CI-APi-ToF and the NAIS data are available from the authors upon request.

Author contribution. JS, NS, LA, TL, JKa and TJ, MS and HJ conducted the measurements, JS and NS handled the data inversion and JS performed the analysis and wrote the paper. JKo, MK and KL designed the study and provided supervision. All of the authors contributed to the discussions of the results and commenting on the paper.

Competing interests. The authors declare that they have no conflict of interest.

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