

We thank both reviewers for their valuable comments. The reviewers' comments are listed below and are followed by our replies (in italics).

Anonymous Referee #1

This manuscript describes analyses of data collected on the abundance of highly oxidized molecules in a forested environment as part of a comprehensive field campaign. Key to the analysis are observations above and below the forest canopy, which, in principle, allows assessment of flux terms applicable to HOMs. The approaches are well-described and appropriate caveats are clearly stated.

The main issue of concern to this reviewer is the use of two instruments for measurement of HOMs (CP-APi-TOF instruments) that were not side-by-side intercompared over the range of molecular and radical species in the laboratory nor in the field. A single sentence (lines 179-181) states that a laboratory intercomparison was conducted with a permeation tube (not stating what molecules were emitted by the tube) and the results showed good agreement with the relative transmission efficiency experiments. In this approach, assumptions were made as to when the two instruments at two heights (1 m and 36 m) should agree. From this, relative sensitivities between the two instruments were derived (pages 7 and 8). The sensitivity ratio of the two instruments ranged from about 2 to more than 10, depending on the m/z values. Such large differences require significantly more experiments and demonstration than presented in this paper, to convince the reader that the conclusions that arise are valid. This reviewer sees this as a fatal flaw in this manuscript. This is a major point that leads to the recommendation of reconsideration of this manuscript after revisions to address this important point. There are also other issues that should be addressed, as described below.

The reviewer is indeed correct to point out this concern. We shared this concern when starting our initial analyses and critically examined the mass spectra from both instruments with this in mind already before proceeding with the analyses presented in the original manuscript. In the process we became convinced that the differences were indeed real, and not purely instrumental artifacts. Unfortunately, we failed to include enough of such data in the manuscript, as both reviewers pointed out. This has now been amended in the revised version, and we believe that we now clearly show that the differences are due to variations in atmospheric composition between the two heights, and not a result of instrumental changes.

The instrument in the tower had been part of the site's continuous measurements since 2014, and the ground instrument was deployed in 2016. It is extremely unfortunate that a direct side-by-side inter-comparison was not done at the time of the deployment, as it would have greatly facilitated the data analysis. However, as a first

step to validate a comparison, we used a permeation tube with trinitrotriazinane, detected as $C_3H_6N_6O_6 \cdot NO_3^-$ (m/z 284) and $(C_3H_6N_6O_6)_2 \cdot NO_3^-$ (m/z 506) located in the HOM monomer and dimer range, respectively, and the same permeation source was connected in the same manner first to one instrument and then to the other. The results supported the increasing relative transmission efficiency (TE) curve presented in Fig. 1.

Now we added these inter-comparison results to Figure 1 and modified the text to:

“Additionally, an inter-comparison between the two instruments with a permeation tube containing trinitrotriazinane ($C_3H_6N_6O_6$) was conducted in the field right after the campaign. The results showed good agreements with the relative TE, lending confidence to the method used here...”

To validate the large differences (nearly an order of magnitude) between observed HOM concentrations during inversion nights, we also added two figures and text in section 4.4 to show more temporal and spectral details of the changes between the instruments. We believe the presented figures unambiguously show that the changes are a result of different chemistry at the two heights due to decoupled layers, rather than e.g. temperature or RH-driven instrumental changes (as suggested by reviewer 2). The added section is inserted below:

“From the measurement side, one major concern was the comparability between our two CI-APi-TOF mass spectrometers. In the worst case, our conclusion might be biased if instrument responses changed due to some parameter that correlated with the observed inversions. The main parameters in this case would be ambient temperature and RH. As both instruments were located in temperature-controlled containers and the sample flow was mixed 1:2 with dry sheath air in the CI-APi-TOF drift tube, neither of these were expected to yield such large changes. However, for confirmation, we compared the detailed spectral evolution during days and nights of the study. Figure 8 shows an example of hourly changes of the ratios between tower and ground HOMs, over a 24h period without nighttime temperature inversion (September 11). During this period, ambient temperatures changed from 19.1 °C (12:00 LT) to 8.8 °C (07:00 LT) at ground level, and from 17.9 °C to 8.1 °C at tower level. Ambient RHs also increased from 72 % to 96 % at ground level, and from 74 % to 98 % at tower level. While some scatter is visible in the 200-300 Th range during some parts of the night, good agreement was observed between the two instruments throughout the night, despite large variability in temperatures and RHs.

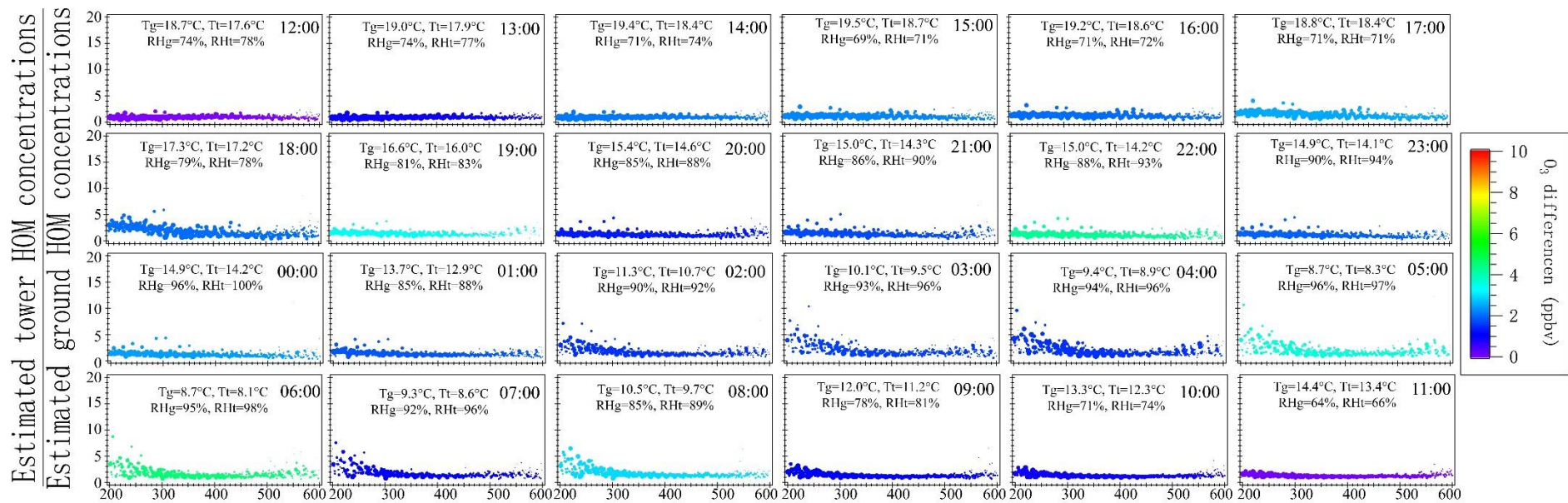


Figure 8 Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 11, 12:00 to September 12, 11:00 (non-inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3_{tower}} - O_{3_{ground}}$). Hourly ambient temperatures at ground (Tg) and tower (Tt) levels, and RH at ground (RHg) and tower (RHt) levels are shown in each subplot.

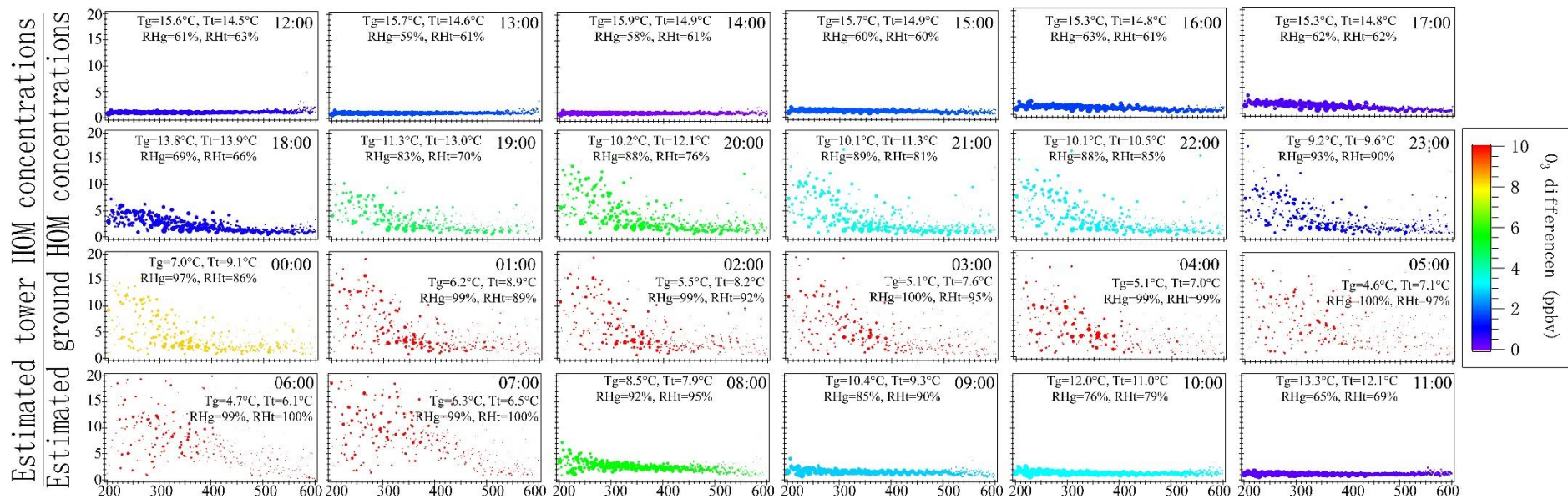


Figure 9 Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 8, 12:00 to September 9, 11:00 (inversion night). Markers are sized by ground HOM concentrations and colored by O_3 difference between tower and ground ($O_{3_{tower}} - O_{3_{ground}}$). Hourly ambient temperatures at ground (T_g) and tower (T_t) levels, and RH at ground (RH_g) and tower (RH_t) levels are shown in each subplot.

In contrast, during a 24h period with nighttime temperature inversion (September 8, shown in Figure 9), the ratios agreed well only during daytime (from 12:00 to 17:00, and 09:00-11:00 on the next day). Between these periods, temperature and RH were most of the time in the same range as on September 11 (when no strong deviations were observed), but now the HOM behavior changed dramatically between the two heights. The ratios increased from ~1 (during daytime) up to ~20 at 07:00 for some of the measured molecules.

Figures 8 and 9 clearly imply that the large differences between ground and tower HOM concentrations were driven by temperature inversions and consequent changes in the composition of the air in the two detached layers. Large changes in HOMs were observed only when the ground temperature was lower than the tower temperature and when the ozone concentration at ground level was several ppb lower. Absolute temperatures or RHs at the two heights were not able to explain the changes. As a concrete example, good agreement was observed at 07:00, September 12, while ambient temperatures were low (ground and tower temperatures were 9.3 °C and 8.6 °C, respectively) and RHs were high (ground and tower RHs were 92 % and 96 %, respectively), but large deviations were found at 20:00, September 8, when higher temperatures (ground and tower temperatures were 10.2 °C and 12.1 °C, respectively) and lower RHs (ground and tower RHs were 88 % and 76 %, respectively) were observed. In other words, neither low temperatures nor high RHs caused large changes to our instruments. Instead, the large discrepancies between the two CI-APi-TOFs were only observed when other key parameters (like ozone) were found to deviate considerably between the two heights.”

Page 2, line 32. Suggest rewording “...attached to the forest floor.”
Modified.

Page 2, line 37. Suggest “This could, in turn, influence interpretation of the growth...”
Modified.

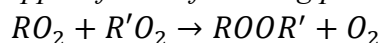
Page 3, line 60. Were the HOM clusters in the laboratory experiments also “naturally charged”?
Yes.

Page 3, line 79. Suggest “...compounds, with masses between...”
Modified.

Page 3, line 84. Suggest "...compounds, with masses between...". In the dimerization of RO₂ radicals, what is the chemical mechanism, and what types of molecules are formed (peroxy radicals, organic peroxides, ROOR, etc.)?

Modified.

The exact chemical mechanism of RO₂ radical's dimerization is still under discussion, and therefore we did not go into details about this in the manuscript. However, recent studies (Ehn et al., 2014; Jokinen et al., 2014; Berndt et al., 2018) have shown strong support for the following pathway:



which is the "HOM dimer" in the manuscript. We also add two more references (Jokinen et al., 2014; Berndt et al., 2018) to the sentence now.

Page 4, line 91. Suggest rewording. Do you mean oxidants of monoterpenes that product HOMs, or oxidants of HOMs producing other molecules or radicals?

Modified. Now the sentence is

"Unsurprisingly, the oxidants producing HOMs (e.g. O₃) were found almost uniformly distributed within the well-mixed daytime boundary layer".

Page 4, line 95. Is the term "sub-canopy" typical used, or would "below canopy" and/or "in canopy" be better?

Modified. Now the three terms are unified as "below the canopy".

Page 4, line 108. It is stated that the lower inlet is at 1.5 m, which is different than stated on page 5, line 131. Suggest making everything consistent.

Modified. The height of lower inlet is ~1.5m.

Page 5, line 118-119. Suggest "...southeast of the site, and from the city area of Tampere..."

Modified.

Page 5, line 124. Should "April" be "August"?

According to the cited references, "April" is correct because nocturnal boundary layer has not been measured in August.

Page 5, line 128-129. Suggest "...deployed at the top..."

Modified.

Page 6, line 138. Suggest rewording "...then converged to the center..."

Modified. Now the expression is "then centered to an ion reaction tube".

Page 6, line 146. Suggest "...stack of ion lenses guided the ions..."

Modified.

Page 6, line 153. Are you missing a summation sign before the “M” in the numerator?

Corrected.

Page 6, line 164-165. While it is true that absolute HOM concentrations are not as important in this work, the relative sensitivity of the two instruments is of critical importance (see earlier comment).

See our first response above.

Page 7, line 180-181. Since the permeation tube experiments could potentially be very important, much more detail needs to be given. What is(are) the compound(s) coming from the permeation tube? What does “good” agreement mean? Can the results be included in Figure 1?

See our first response above.

Page 7, line 184. How is the instrument tuned for maximum sensitivity at the largest masses?

The sensitivity of a CI-APi-TOF can be tuned to maximize ion throughput at different mass ranges by varying voltages and radiofrequencies applied to the guiding quadrupoles in the instrument. Especially the quadrupole settings can increase the throughput at larger masses at the expense of the smaller masses. In this study, the tower CI-APi-TOF was tuned for maximum sensitivity at the highest masses. We assumed a detailed discussion on this would become too technical in the manuscript, but we now reformulated the sentence to:

“...the tower CI-APi-TOF had been tuned for higher sensitivity at the larger masses”.

Page 8, Figure 1. Is there a theoretical reason to fit the data with a power law, or did that simply provide a reasonable representation?

No, it just provided a reasonable representation.

Page 8, lines 195 to 197. It is concerning that the various controlling parameters were not measurements at precisely the same heights as the HOM measurements. It is also concerning that these other measurements were 100 m away. Can you provide information that these differences did not affect the conclusions of this study?

Thousands of different parameters are measured at the SMEAR II station, and therefore it is inevitable that not all of them are co-located. We could not totally rule out the influence from other micrometeorological processes occurring in the space between the different locations/heights, however, their contributions should be minor compared to the dramatic changes observed in HOM concentrations. This matter was also discussed in the study limitation part (section 4.4):

“...the contribution from the potential micrometeorological processes in the layer between 1.5 m and 4.2 m (between the sampling heights of the ground HOMs and other parameters) could not be estimated with the current experiment design (i.e., only two measurement heights). Similarly, the influence from horizontal advection could not be entirely ruled out as a contributor to the reduced ground-level HOM concentrations (and other significantly changed species), because of the possible horizontal inhomogeneity of HOM precursors and oxidants below the canopy. However, our conclusion was confirmed by the incompatibility between the increasing ground MT and CO₂ concentrations and the advection hypothesis (i.e., all species would show similar tendencies if advection played a major role), indicating the influence of horizontal and vertical advection is probably minor when compared to the increasing sink.”

It could also be added that the main conclusion of our manuscript is that fixed-point ground level observations should not automatically be assumed to always represent the situation at higher altitudes. If large discrepancies were taking place also when moving ~100m in the horizontal direction, this would only make our conclusions even more important.

Page 8, line 200. Suggest “...with a lower detection limit...”
Modified.

Page 8, line 202. Suggest “...that had a lower detection limit...”
Modified.

Page 8, line 205. Suggest “...lower detection limit of the NO_x analyzer was...”
Modified.

Page 9, line 209. Also concerning that the aerosol measurements were not made at the same heights at the HOM measurements. What impact could this have?
No significant impact, we only used aerosol measurements to calculate CS, and used CS to indicate air mass change in our case studies, which will not influence our conclusion. The aerosol particle lifetimes are on the order of days, and therefore minimal changes are expected between the two heights, as has been verified in earlier aerosol studies at the site.

Page 9, line 216. Suggest “...averaging intervals, except for the MT (in 1-hour averaging intervals).”
Modified.

Page 9, line 227-229. Suggest “The mean air temperature and RH observed at ground level were..., and at the tower level were...”
Modified.

Page 9, line 230-231. Suggest providing statistics for temperature, RH, and O₃ separately for daytime and nighttime.

Modified.

Page 9, line 222 and page 10, line 223. This statement is confusing. The NO_x detection limit is 50 pptv (line 205), so how does this relate to mean +/- standard deviation values given. Need a bit more text to describe what was done statistically, and what the results say.

The text was changed to:

“The O₃ concentrations measured at ground and tower levels were 21 ± 8 ppbv and 25 ± 6 ppbv, respectively.”, and “...the mean NO_x concentrations were mostly around the reported detection limit at 0.4 ± 0.4 ppbv (ground) and 0.4 ± 0.5 ppbv (tower), ...”

Page 20, line 235-236. Suggest “...were generally higher than those above...”

Modified.

Page 11, line 242. Since the transmission efficiencies are not used in the reduction of the data, this reviewer disagrees with the statement that the sum of the signals between m/z 200 to 600 represents the total HOM concentration. This needs some reworking. If the transmission efficiencies are not known, then suggest not giving HOM concentrations, but perhaps HOM signals.

We had also considered this option, but ultimately concluded that since we know roughly the HOM concentrations, it would be more useful for a reader to compare actual concentrations, albeit they have high uncertainty. We tried to highlight this uncertainty in section 3.2. by writing:

“an uncertainty of -50%/+100%, was used in calculating the HOM concentrations for both instruments. Ultimately, the absolute HOM concentrations in this work are of secondary importance, as we focus on the relative comparison of HOM concentrations measured at different heights.”

And

“In comparison to the direct determination of TE (Heinritzi et al., 2016), this method increases the uncertainty in the quantification of HOM concentrations. However, as mentioned, a more accurate knowledge of the exact HOM concentrations would not influence the main findings of this study.”

We now try to even further emphasize this uncertainty by changing all the “total HOM concentration” to “estimated total HOM concentration”, and adding below text to give a clearer statement in the manuscript:

“an uncertainty of at least -50%/+100%, was used in calculating the HOM concentrations for both instruments. Ultimately, the absolute HOM concentrations in this work are of secondary importance, as we focus on the relative comparison of HOM concentrations measured at different heights.”

Page 11, line 246-248. Are the statistics for all the data, or just daytime or nighttime? The value after +/- is presumably the standard deviation. This needs to be stated. In the last sentence “these differences” are mentioned, but it needs to be specifically stated which differences are being referred to (e.g. differences in the means above and below (fairly small), differences in the medians (larger), etc.)? *The statistics were determined basing on the whole data. The value after the symbol “±” had been defined as (1σ standard deviation, page 9, line 230) in section 4.1. Additionally, there was an ~55% difference in mean values (~71% in median) between the two heights, which is quite large.*

Now the sentence is modified to:

“The causes of these differences (~ 55% in mean and ~71% in median) frame the upcoming discussion.”

Page 11, line 252. Suggest adding statistics to demonstrate HOM concentrations at the two heights were not different during the day.

Added. Now the sentence is:

“The total HOM concentrations at the two heights were not different during the day (mean ± 1σ standard deviation and median concentrations of $4.1 \pm 2.3 \times 10^8 \text{ cm}^{-3}$ and $3.6 \times 10^8 \text{ cm}^{-3}$ at ground level, $4.3 \pm 2.6 \times 10^8 \text{ cm}^{-3}$ and $4.0 \times 10^8 \text{ cm}^{-3}$ at tower level), which ...”

Page 11, line 254. Suggest a figure showing that the ratio (or some other metric) of the HOM concentrations at the two heights did not change with time during the day.

Added, see Figure 8 and Figure 9.

Page 11, line 257. Suggest including statistics and time dependence for the two heights (as above) for nighttime data.

Added, see Figure 8 and Figure 9.

Page 11, line 258. Suggest showing the temperature difference between the two heights in Figure 2 to help clearly show when there are temperature inversions.

We have changed the temperature in Figure 2 from liner scale to log scale, which we think serves the same purpose.

Page 11, line 261 and Figure 3. Suggest giving statistics to support the statement that there is good agreement around midday.

Added. Now the sentence is:

“...representing the concentrations around noontime ($R^2 = 0.89$)...”

Page 11, line 264 and Figure 3. Suggest giving statistics for nighttime HOM concentrations to support the statement.

Added. Now the sentence is:

“The points indicating the nighttime total HOM concentrations were scattered ($R^2 = 0.28$)...”

Page 12, line 270. Suggest “...shows the mean mass spectra...” and “...UMR, for m/z 200...” and remove “HOM measurements”

Modified.

Page 12, line 283. Suggest “...strength and/or source-sink...”

Modified.

Page 14, line 292. Suggest adding “likely” or “probably” in “...level are likely influenced by...”.

Modified.

Page 14, line 294-296. Suggest “...the potential impact of such micrometeorological phenomena on ground level HOMs, for the nights during the campaign without precipitation or instrument failure, were selected...”

Modified.

Page 14, line 297. Suggest “...based on the occurrence of temperature inversions...”

Modified.

Page 14, line 299. Suggest “...type category consisted of 6 nights...”.

Modified.

Page 14, line 301. Suggest “...lower than tower...”

Modified.

Page 14, line 307. Suggest “...above the canopy was relatively...”

Modified.

Page 14, line 310. Is it known that there are higher VOC emissions near the ground within forest canopies? A reference or two would be good here.

Rantala et al., (2014) is added to the text.

Page 14, line 315. Suggest “...similar in both categories and heights...”

Modified.

Page 16, Table 1. This reviewer found the gray bars in the table (not the titles) confusing. Suggest configuring the table differently.
Modified.

Page 17, line 344 and Table 2. Were these categories done for all conditions, all times (looks like it is nighttime), and both heights?
Yes, this table only included the nighttime data and both heights.

Page 17, line 363. Suggest “Roughly, Ri values in excess...” and “...stratified conditions appreciably...”.
Modified.

Page 17, last paragraph and Figure 5. Were these data for the ground level measurements?

No, both ground and tower measurement data were involved in this paragraph and Figure 5, except for CS (determined based on the data measured at 8m a.g.l.) which was only used as an indicator of air mass change. The bulk Richardson number (Ri) is a scale of the air stability, and was calculated using the meteorology data of both ground and tower levels measurements. A detailed description was already given in section 4.3.2. We modify below texts to make a clearer statement in the manuscript:

“Figure 5b shows the time series of the trace gases, MT, and HOM groups of both ground and tower measurements during an “inversion night” case (September 8-9, from 21:00 to 03:00).”

And

“The parameters measured at tower level were not significantly affected by strong Ri fluctuations throughout the night, in contrast, significant variations were observed at ground level.”

And the caption of Figure 5:

“Figure 1 (a) Time series of ground and tower concentrations of CO₂, NO_x, O₃, MT, and selected HOM groups in the selected “non-inversion night” (September 11), and (b) “inversion night” (September 8). Ri is calculated with the meteorology data of ground and tower levels. CS is determined based on the aerosol data measured at 8 m above ground level.”

Page 19, line 381. Suggest “...significant decreases after midnight.”
Modified.

Page 19, line 387. Suggest “...HOM concentrations might...”

Modified.

Page 19, line 388. Suggest "...but also due to some other processes such as additional losses."

Modified.

Page 19, line 391. Suggest giving the location of the Alekseychik et al study.

Modified. The study was conducted in the same SMEAR II station. Now the expression is:

"A previous study by Alekseychik et al., (2013) at SMEAR II station showed that..."

Page 19, line 392. Suggest "...Ri conditions in the..."

Modified.

Page 19, line 396. Suggest "...in significantly different O3..."

Modified.

Page 19, line 397. See earlier comment about "sub-canopy".

Modified.

Page 20, top paragraph. This reviewer found the use of T1, T2, etc confusing since capital T is usually reserved for temperature. Suggest using different symbols.

Modified. Now change to "N".

Page 20, line 418. Suggest "Note that these..."

Modified.

Page 20, line 421. Suggest "area-to-volume ratio..."

Modified.

Page 20, line 424. See earlier comment about "sub-canopy".

Modified.

Page 22, line 452. Suggest "...however, such an analysis might only indicate the major..."

Modified.

Page 22, line 453. Suggest "...holistic view of the entire mass spectrum..." or some other rewording.

Modified.

Page 23, line 461. Suggest "...large differences could..."

Modified.

Page 23, line 463. Suggest "...disappeared on the..."
Modified.

Page 23, line 468. Suggest "...limitations still exist in this..."
Modified.

Page 23, line 472. Suggest "...influence of horizontal advection could not be entirely ruled out as a contributor to..."
Modified.

Page 23, line 473. Suggest "...HOM concentrations...". Suggest rewording "largely changed species"
Modified. Now the sentence is:

"... HOM concentrations (and other significantly changed species)"

Page 23, line 473. Suggest "...because of possible horizontal..."
Modified.

Page 23, line 477. Suggest "...advection is probably minor..."
Modified.

Page 23, line 479. Suggest "...evidence is still needed..."
Modified.

Page 23, line 479-280. Suggest "...which highlights the need for...". Also define "joint vertical-planar HOM studies".
Modified, and now the sentence is:

"...which also highlights the need for joint vertical-planar HOM studies, measuring both vertical and horizontal distribution of HOM concentrations."

Page 23, line 484. Suggest "...IBAIRN campaign that took place in September 2016."
Modified.

Page 24, line 486. Suggest "...that influence the abundance and trends of HOMs..."
Modified.

Page 24, lines 505-507. Suggest "...close to the ground, and the effect of boundary layer..." and "...processes to HOM concentrations have..."
Modified.

Page 24, line 509. Suggest "...HOM concentrations found in nocturnal inversion situations."

Modified. Now the expression is:

"...reduced HOM concentrations in the inversion nights."

Page 24, line 510. Suggest "Influence of boundary..."

Modified.

Page 27, line 582. There is a typo in this reference.

Modified.

References:

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

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J. and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, 506(7489), 476–479, doi:10.1038/nature13032, 2014.

Jokinen, T., Sipilä, M., Richters, S., Kerminen, V.-M., Paasonen, P., Stratmann, F., Worsnop, D., Kulmala, M., Ehn, M., Herrmann, H. and Berndt, T.: Rapid Autoxidation Forms Highly Oxidized RO₂ Radicals in the Atmosphere, *Angew. Chemie Int. Ed.*, 53(52), 14596–14600, doi:10.1002/anie.201408566, 2014.

Rantala, P., Taipale, R., Kajos, M. K., Patokoski, J., Ruuskanen, T. M., Rinne, J. and Aalto, J.: Continuous flux measurements of VOCs using PTR-MS — Reliability and feasibility of disjunct-eddy-covariance, surface-layer-gradient, and surface-layer-profile methods, *Boreal Environ. Res.*, 19, 87–107, 2014.

Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A. and Curtius, J.: Characterization of the mass-dependent transmission efficiency of a CIMS, *Atmos. Meas. Tech.*, 9(4), 1449–1460, doi:10.5194/amt-9-1449-2016, 2016.
Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M. and Hansel, A.: Accretion Product Formation from Self- and Cross-Reactions of RO₂ Radicals in the Atmosphere, *Angew. Chemie Int. Ed.*, 57(14), 3820–3824, doi:10.1002/anie.201710989, 2018.

Anonymous Referee #2

The article by Zha et al. touches on important but challenging issues of how the extremely low volatility, highly oxidized molecules (HOMs aka ELVOC) behave below and above the tree canopy. The article is generally clear and makes many confident insights into the atmospheric variability of these molecules. Because these molecules have high propensity to form SOA, such measurements are needed and potentially valuable. However, I would have some important reservations to this version of the manuscript about the data interpretation and QC/QA, but hopefully, this can be successfully addressed by the authors.

Major

1) Two heights were chosen for measurements of HOMs by two different CI-API-TOF instruments. Although I agree with the other reviewer that this might be regarded as a flaw, I think it does not have to be a critical flaw as long as there is a substantial effort to ensure that the two instruments were in perfect agreement. I am surprised why a portion of measurements was not conducted at the same height (either ground or tower) by both instruments side by side first before moving on to measuring at two heights. It is unfortunate because the collocated measurements would help to ensure that the data reported by two instruments are indeed identical. I am concerned that it might be difficult otherwise to demonstrate this, because there are numerous factors that may affect the agreement between two different instruments apart from the relative transmission. For example, fragmentation, clustering, declustering, or other processes modulated by changes in ambient temperature and humidity may have differed as a function of day, as a function of height, and over longer time scales in either or both instruments. It is therefore really difficult to get convinced if the differences are necessarily because of the height and not because of the differences in each instrument's quantification. A single point laboratory comparison of just the relative transmission of two instruments does not seem sufficient, because of the inability of assessing the factors which change over time. It would be ideal to calibrate regularly the instruments independently and assess separately the deviation from the theoretical transmission of the TOFs like in Heinritzi et al. (2016). Then you could compare the datasets and see how consistent they would be in the middle of a day and at night.

We understand the reviewer's concern about the comparability of the two CI-API-TOF mass spectrometers, and hope that we addressed this concern adequately in the response to reviewer 1. As a specific response here, the reviewer suggested temperature and humidity as two factors that might cause changes to the response of

the CI-APi-TOFs. We believe that Figures 8 and 9, and the corresponding text, that were added in the revised manuscript clearly show that the instruments agree well over a wide range of temperatures and humidities. The only times the instruments show a large discrepancy is when there is a temperature inversion and also key parameters that are known to influence HOM loadings (e.g. ozone) also show large deviations between the two heights.

Finally, if the reviewer's concern was validated, and small changes in ambient temperature or RH would cause the observed changes of ~one order of magnitude through changes in instrument response, it would call into question all published data from these instruments, not only our manuscript. The CI-APi-TOF mass spectrometer has been deployed in very different environments, such as forests, mountain tops, and coastal areas (Bianchi et al., 2016; Kürten et al., 2016; Sipilä et al., 2016; Yan et al., 2016), and no evidence for such erratic behavior has been suggested.

2) Eq. 1 is only valid if the conditions in the reaction chamber or TOF chamber have not changed. Small variations in pressure, temperature or humidity could affect the calibration coefficient. It would be inappropriate to expect that if you set the collision rate the same for all the ions, the relative consistency in two instruments will be the same, because the sensitivity can change over time also because of the drift parameters and resulting issues such as different fragmentation which would not be accounted for by the single transmission correction. It is therefore recommended to take zeros and calibrations of the instruments frequently and none of these are shown except that permeation device is mentioned.

We hope that most of these concerns were addressed in the new Figures 8 and 9. As also discussed in our earlier responses, HOM concentrations were just relatively quantified with Eq. 1, as we were not interested in the absolute HOM concentrations, but more cared about the comparability between the two CI-APi-TOF mass spectrometers. The relative transmission could be deduced from any noon-time, well-mixed period, and it stayed quite constant throughout the measurement period.

We also calculated the ambient pressure difference between ground and tower level, and find it unlikely that such small ambient pressure changes (variation was 4.05-4.28 hPa between ground and tower level) could result in ~20 times differences in HOM signals.

3) I understand that the authors did not seem concerned about the absolute quantification (L165-166) but even the relative quantification is uncertain if one of the instrument was affected by different conditions or its sensitivity drifted throughout a day. It is unclear how the instruments were housed and if the temperature inside the

instruments were monitored and if it was consistent at the two heights. A visual schematic would be useful. One way around could be to either add a period of collocated measurements for a few days and compare the range of compounds or show how stable baselines, sensitivities, and transmissions, were throughout the measurement period if you did regular calibrations.

Most of these comments on inter-comparability have been addressed already in our responses. We added the following text in section 3.2 about how the instruments were housed and their working conditions:

“Both instruments were working in rooms with air-conditioning and room temperatures controlled at 25 °C.”

As also discussed earlier, although they would have been very useful. we can obviously not anymore produce any collocated measurements.

4) Why do you assume a noon period should have identical HOMs concentrations at two heights? I thought these were the first measurements of HOMs at two heights or can you provide a reference? Again, I am surprised that this period was chosen for transmission comparison instead of collocating the two instruments for a longer period. I am not convinced that it is fair to assume that all the HOMs will have no concentration gradient during a day. I am worried that if the HOMs are lost more rapidly at the surface the relative transmission ratio between the instruments may be biased towards larger masses which could be expected to be lost as a function of mass-dependent volatility which could mimic the duty-cycle and transmission related mass discrimination.

We agree with the reviewer that the vertical gradients of HOMs is likely not zero. However, we believe that it is a fair assumption that any such gradient would be small and its influence limited. During noon-time, there is very efficient vertical mixing taking place, and both the main sources (oxidants and VOCs) and sinks (aerosols) have very small gradients between the two measurement heights. While the ground and the canopy are also sink terms for HOM, the canopy is roughly mid-way between the measurement levels.

Additionally, Figure R1 shows the correlation between the normalized (to reagent ions) noontime tower and ground sulfuric acid (SA) signals (before correcting with relative TE) during the campaign. Due to SA's extremely low volatility and high diffusivity, it should have the largest gradient among all the measured compounds. However, they agreed very well and ground SA signals were only ~20% lower than tower signals, suggesting vertical gradient would not significantly affect our relative transmission curve. Moreover, vertical gradient would be the smallest during noontime and larger during night (because of the lower turbulence mixing), but good agreements were still found during the night of September 11 (Figure 8), between

ground and tower HOM measurements. Though the ratios were a bit higher in lower mass range (200-300 Th) during this non-inversion night, they were still much lower compared to September 8 (Figure 9, temperature inversion night), suggesting the large differences between ground and tower HOMs were not mainly from vertical gradient of HOMs.

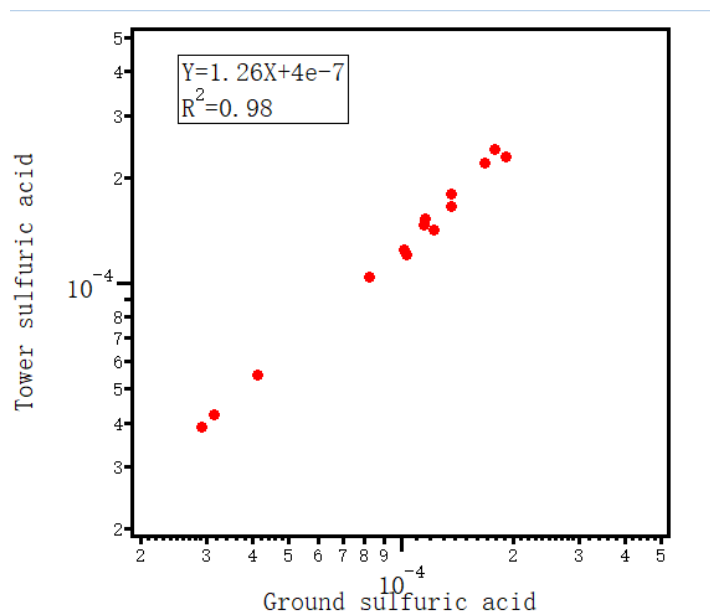


Figure R1 Correlation between all the noontime (12:00 LT) ground and tower SA signals (1-hour averaged, normalized to reagent ions) during campaign.

Finally, the extent of the scatter in Fig. 1 is a clear indication that the governing parameter is indeed the molecular mass. While there is a correlation between molecular mass and volatility, the extent of the scatter in the plot would most likely increase dramatically if the volatility would be the governing parameter. Compare for example that a molecule with the same elemental composition, e.g. $C_{10}H_{16}O_8$, can have isomers with orders of magnitude differences in vapor pressure (Kurtén et al., 2016). Therefore, the data clearly indicates that the mass-dependent transmission is more likely to explain the relative differences during noon-time than different HOM sink parameters.

5) Fig. 2 shows a good agreement for HOMs during noon and not so good otherwise. This relative scaling seems rather arbitrary and not completely unsurprising given the data were normalized using Figure 1 which was derived for the noon time. I am skeptical if these differences really represent the effect of different heights. The differences are huge because the data are shown on a log scale. I would recommend showing the comparison on a linear scale.

For the first part of the comment, we have addressed these issues earlier. As for the scale, since we are more interested in the relative difference between ground and

tower measurements and not the absolute HOM concentrations, we find it more reasonable to show the ground and tower HOM concentrations in log scale. The absolute differences are easy to read out from the graph, and we do not therefore think that there should be any risk for misinterpretation of the plot.

6) Overall, I was missing a stronger link to chemical and physical properties of HOMs and a deeper insight into individual classes and not just the total sum of HOMs. In particular, the transport could be molecule specific and may not be unified across the full range of HOM vapor pressures. I feel that the dataset has a much higher potential for teaching a reader about the behavior of HOMs. The current version of the paper gives an impression of semiquantitative and speculative in terms of HOM vertical behavior. I am not convinced by looking at temperature variations (Fig. 2) that the inversion hypothesis is strong. There is much attention directed to the general remarks about advection and turbulent quantities which is difficult to infer how they affect HOMs without direct flux measurements of HOMs by eddy covariance.

We certainly agree with the reviewer that this is a very rich data set and future work will look more into molecule-level differences. As we believe we have shown in these responses, the concentration differences are driven by decoupling of layer between the two measurement heights, but as is clear from the scatter in Fig. 9, the chemistry is changing drastically. But we also feel that it would go out of scope for this study to involve detailed discussions on the HOM chemistry in addition to all other topics covered. Additionally, we do show several different types of HOMs in Figure 5, and their main formation pathways were also listed in Table 2 in the manuscript.

The existence of temperature inversion in the boreal forest environment has been proven in many studies, and a small temperature inversion could result in decoupled layer formation and have significant influences to O₃, monoterpene and CO₂ concentrations (Rannik et al., 2009, 2012; Alekseychik et al., 2013; Chen et al., 2018). Since HOM concentrations have a strong dependence on O₃ and MT concentrations, it would inevitably be affected by temperature inversion. However, the potential importance of micrometeorology in HOM measurements had yet been recognized by most of the community, prompting us to publish our findings without further delays.

Minor

7) I wonder why you are adopting the HOM nomenclature and not ELVOC. Mentel et al. (2015) suggested that the latter is more appropriate when referring to atmospheric impacts and HOMs if the focus is more on compounds' structure. As you are focusing on the behavior in the atmosphere I think considering volatilities could make sense.

Are you sure that all the molecules you report are highly oxidized (high carbon oxidation state)? That would not be true for compounds such as cyclic and linear siloxanes which should be subtracted from the HOMs class.

In most studies where HOM or ELVOC have been used, they have been effectively defined in the same way, as the oxidized organic compounds that are detected by a nitrate ion based CI-APi-TOF (e.g. Ehn et al., 2014; Kirkby et al., 2016). However, according to a recent study by Kurtén et al., (2016), there is a large difference between ELVOC and HOM, and HOM measured with nitrate ion based CI-APi-TOF spans a wide range of volatilities (Kirkby et al., 2016), not only the ones with extremely low volatilities (ELVOC). Therefore, HOM is a better nomenclature for our study, since we can actually infer the amount of oxygen in the molecules, while assessing the volatility would require many assumptions. The reviewer also suggested that variations in volatility could cause differences in the expected gradients, but if all detected molecules were ELVOC, they would all behave identically. Note also that we use the term “highly oxygenated” and not “highly oxidized”, and thus are not inferring an oxidation state, rather just the oxygen content.

There are also molecules in the studied mass range that are not very highly oxygenated, but the amount of these is small. This is a feature of our instruments, as the reagent ion (NO_3^-) of our CI-APi-TOF mass spectrometer is very selective and tends to charge molecules with high oxygen content (mostly with six or more O-atoms).

8) Figure 3 does not provide much information when it is colored by the time of day. For the reasons mentioned above the scatter outside of the noon hour might not necessarily be because of less good mixing other than at noon. One could possibly learn more if the data were colored by potential temperature or relative humidity. *We think this figure is quite important and needs to be colored by the time of day to show that noontime data is always well-correlated (which e.g. the reviewer questioned in comment 4). Since the relative transmission curve was determined based on the noontime data on September 9, Figure 3 shows that there were good agreements between ground and tower measurements during every day of the campaign, and large differences were usually observed during night.*

9) Figure 4c, the scatter looks weird that it is so much shifted (by an order of magnitude) but still reasonably correlated. I wonder if it is possible to evaluate any volatility dependent difference but it seems that it might be difficult if there is a high uncertainty in transmission differences.

We are not sure if we interpret the reviewers comment correctly, but we think the reviewer may have interpreted the figure as a correlation between the timeseries of ground and tower HOMs, while it in fact shows the correlation between each ion in

the mean ground and tower spectra. In any case, since Figure 4b and 4c ultimately contain the same information as Figure 4a, we decided to remove these two figures from our manuscript completely.

10) Figure 1 is technical and could be moved to SI. I would suggest to replace it by separate individual curves of theoretical and measured transmissions from each instrument and the datasets should be corrected individually.

We believe Figure 1 is important for readers to understand the concept of this study, it is the basis to compare ground and tower HOM measurements. As also both reviewers' comments circled around this scaling, we feel it is critical to have it easily accessible in the main text. We also cannot replace it with any measured transmission curves as the reviewer suggests, since such do not exist. Similarly, we are not aware of any method to derive theoretical transmission curves as such would need to take into account all dimensions, flows, the ~30 voltages and the two radiofrequencies inside the APi-TOF. Therefore our only option remains to do the scaling as shown in Fig. 1, which we believe we have validated in our responses and the new version of the manuscript.

Technical

L67 space between “)” and “from”.

Corrected.

Table 1, ensure the number of significant figures is consistent and as appropriate.

Corrected.

Table 2, if there is only one N atom in a molecule there is no need to add 1. For example, C₁₀H₁₅O₁₁N₁ should be C₁₀H₁₅O₁₁N.

Corrected.

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Vertical characterization of Highly Oxygenated Molecules (HOMs) below and above a boreal forest canopy

Qiaozhi Zha¹, Chao Yan¹, Heikki Junninen¹, Matthieu Riva¹, Juho Aalto¹, Lauriane Quéléver¹, Simon Schallhart¹, Lubna Dada¹, Liine Heikkinen¹, Otso Peräkylä¹, Jun Zou², Clémence Rose¹, Yonghong Wang¹, Ivan Mammarella³, Gabriel Katul^{4,5}, Timo Vesala¹, Douglas R. Worsnop^{1,6}, Markku Kulmala¹, Tuukka. Petäjä¹, Federico Bianchi¹, and Mikael Ehn¹

¹ Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

² CMA-NJU Joint Laboratory for Climate Prediction Studies, Institute for Climate and Global Change Research, School of Atmospheric Sciences, Nanjing University, Nanjing, China

³ Department of Physics, University of Helsinki, P.O. Box 48, 00014 Finland

⁴ Nicholas School of the Environment, Duke University, Durham, North Carolina, USA

⁵ Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina, USA

⁶ Aerodyne Research, Inc., Billerica, MA 01821, USA

Abstract

While the role of highly oxygenated molecules (HOMs) in new particle formation (NPF) and secondary organic aerosol (SOA) formation is not in dispute, the interplay between HOM chemistry and atmospheric conditions continues to draw significant research attention. During the Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget (IBAIRN) campaign, profile measurements of neutral HOM molecules below and above the forest canopy were performed for the first time in the boreal forest SMEAR II station during September 2016. The HOM concentrations and composition distributions below and above the canopy were similar, supporting a well-mixed boundary layer approximation during daytime. However, much lower HOM concentrations were frequently observed at ground level due to the formation of a

32 shallow decoupled layer below the canopy. Near ground HOMs were influenced by the
33 changes in the precursors and oxidants, and enhancement of the loss on surfaces in this
34 layer, while the HOMs above the canopy top were not significantly affected. Our
35 findings also illustrate that near-ground HOM measurements conducted in strong stably
36 stratified conditions might only be representative of a small fraction of the entire
37 nocturnal boundary layer. This **could**, in turn, influence the growth of newly formed
38 particles and SOA formation below the canopy where a large majority of measurements
39 are typically conducted.

40 **Introduction**

41 Highly oxygenated molecules (HOMs), a sub-group of the oxidation products of
42 volatile organic compounds (VOCs) identified by their high oxidation states, have been
43 recognized as important precursors for organic aerosol in the atmosphere (Ehn et al.,
44 2014). They have also been found to enhance new particle formation (NPF) and growth
45 (Kulmala et al., 2013; Zhao et al., 2013; Ehn et al., 2014; Bianchi et al., 2016; Kirkby
46 et al., 2016; Tröstl et al., 2016). The importance of HOMs has been confirmed in
47 ambient environments, especially in monoterpene-dominated regions such as the boreal
48 forest (Kulmala et al., 2013; Ehn et al., 2014), but also in high altitude mountain regions
49 (Bianchi et al., 2016) and in rural areas (Jokinen et al., 2014; Kürten et al., 2016). In
50 laboratory studies, HOM formation has been observed from various precursor
51 molecules (Ehn et al., 2017), including both biogenic and anthropogenic emissions.

52

53 The direct observation of HOMs has only recently become possible, following the
54 developments of the Atmospheric-Pressure-interface Time-Of-Flight (APi-TOF,
55 measures the charged HOM clusters) (Junninen et al., 2010) and Chemical Ionization
56 Atmospheric-Pressure-interface Time-Of-Flight (CI-APi-TOF, measures the neutral
57 HOM molecules) (Jokinen et al., 2012) mass spectrometers. Ehn et al. (2010) and
58 Bianchi et al. (2017) found that the naturally charged HOM clusters could be observed

59 every night in boreal forest during spring. Out of the observed ambient mass spectra, a
60 significant part could be reproduced in a chamber by introducing the monoterpene α -
61 pinene ($C_{10}H_{16}$, the major biogenic VOC in the boreal forest) and ozone (O_3) (Ehn et
62 al., 2012).

63

64 Further investigations of HOM formation chemistry have been done in both laboratory
65 and field studies. Based on current understanding from laboratory experiments, the
66 formation of HOM molecules involves three main steps: 1) initial formation of peroxy
67 radicals (RO_2) from VOC oxidation; 2) RO_2 auto-oxidation, that is, the isomerization
68 of the RO_2 via intramolecular H-shifts and the subsequent oxygen (O_2) additions; and
69 3) radical termination, forming closed-shell molecules (Crouse et al., 2013; Ehn et al.,
70 2014; Jokinen et al., 2014, 2016; Rissanen et al., 2014; Mentel et al., 2015). In the
71 atmosphere, HOM formation studies are complicated by the plethora of different
72 compounds and processes taking place. However, recent ambient measurements
73 together with factor analysis were able to shed light on the HOM formation pathways
74 in the boreal forest (Yan et al., 2016). They showed that the majority of the daytime
75 production of HOMs was from reactions initiated by the oxidation of monoterpenes
76 (MT) with hydroxyl radical (OH) or O_3 . The RO_2 after auto-oxidation was either
77 terminated by hydroperoxyl radical (HO_2) or self-termination (Orlando and Tyndall,
78 2012), to form a non-nitrate HOM monomer ($CHO_{monomer}$, mainly C_9 and C_{10}
79 compounds, with masses between 290-450 Th after clustering with the charging ion
80 (NO_3^-) of the instrument); or reacting with nitrogen oxides (NO_x) to form an
81 organonitrate HOM monomer ($CHON_{monomer}$). During nighttime, MT were mainly
82 oxidized by O_3 and NO_3 radical. Furthermore, due to the lower nocturnal HO_2 and NO_x
83 concentrations, besides the production of $CHON_{monomer}$, the RO_2 products could also
84 react with another RO_2 to form a non-nitrate HOM dimer (CHO_{dimer} , mainly C_{16-20}
85 compounds, with masses between 450-600 Th after clustering with NO_3^-) or an
86 organonitrate HOM dimer ($CHON_{dimer}$), depending on the oxidants of the RO_2 radical.

87 (Ehn et al., 2014; Jokinen et al., 2014; Yan et al., 2016; Berndt et al., 2018).
88
89 Beyond those chemical pathways, varied meteorological conditions are also factors
90 influencing the MT and oxidants at different heights above the forest floor.
91 Unsurprisingly, the oxidants **producing** HOMs (e.g. O₃) were found almost uniformly
92 distributed within the well-mixed daytime boundary layer (Chen et al., 2018). In
93 contrast, the nocturnal boundary layer was shallow with stability regimes that depended
94 on radiative cooling within the canopy and turbulent shear stresses at the canopy top.
95 In Hyytiälä, the depletions of O₃ **below the** canopy were frequently observed during
96 nighttime, while the O₃ above the canopy was less affected. The MT concentration at
97 ground level increased when O₃ was depleted (Eerdekens et al., 2009). The
98 inhomogeneous distribution of the precursors and oxidants below and above the canopy
99 might further impact nocturnal HOM distributions, which frames the scope of this study.
100 Until now, all CI-APi-TOF deployments have been at ground level, and the main
101 subject of inquiry here is the vertical information on HOMs and the role of
102 meteorological condition in shaping them. A characterization of the HOMs at different
103 heights provides a decisive advantage in disentangling the role of non-uniform mixing
104 within the atmospheric layers impacted by strong thermal stratification, especially
105 inside the canopy volume.
106
107 The first measurements of the HOM concentrations at two different heights (36 m and
108 1.5 m a.g.l.) during September 2016 are presented and discussed. The influence of
109 boundary layer dynamics on the HOMs at these different heights are explicitly analyzed
110 and characterized in conjunction with auxiliary turbulence and micrometeorological
111 measurements.

112 **Experimental**

113 **1.1 Measurement site description**

114 The measurements were performed at the SMEAR II station (Station for Measuring
115 Ecosystem–Atmosphere Relations) in the boreal forest in Hyytiälä, southern Finland
116 (61°51' N, 24°17' E, 181 m a.s.l., Hari and Kulmala, 2005; Hari et al., 2013) during
117 September 2016. There is no large anthropogenic emission source at or near the site.
118 The closest sources are the two sawmills ~5 km southeast of the site, and from the city
119 area of Tampere (~60 km away). The forest surrounding the station is primarily Scots
120 pine with a mean canopy height of ~17.5 m (Bäck et al., 2012). The planetary boundary
121 layer height at the SMEAR II station has been determined from previous studies using
122 radiosondes (Lauros et al., 2007; Ouwersloot et al., 2012) and balloon soundings
123 (Eerdeken et al., 2009). Roughly, these heights span some 400 m (March) to 1700 m
124 (August) at noontime, and 100 m (March) to <160 m (April) at midnight.

125 **1.2 Instrumentation**

126 Concentration of HOM molecules were measured with two nitrate-ion based CI-APi-
127 TOF mass spectrometers. The CI-APi-TOF measuring at higher altitude was deployed
128 at the top of a 35 m tower located ~20 m horizontally from the ground measurement
129 location. Both instruments were working in rooms with air-conditioning and room
130 temperatures controlled at 25 °C. The inlets of the two instruments were pointed to the
131 southeast direction and fixed at ~36 m and ~1.5 m above ground. The tower
132 measurement is about twice the canopy height, which is still within the roughness
133 sublayer of the forest (Raupach and Thom, 1981). The instrument setup of the two CI-
134 APi-TOF mass spectrometers were similar. In brief, the CI-APi-TOF was the
135 combination of a chemical ionization (CI) inlet, and an atmospheric pressure interface
136 time-of-flight (APi-TOF) mass spectrometer (Aerodyne Research Inc., USA, and
137 Tofwerk AG, Switzerland). The ambient air was first drawn into the inlet with a sample

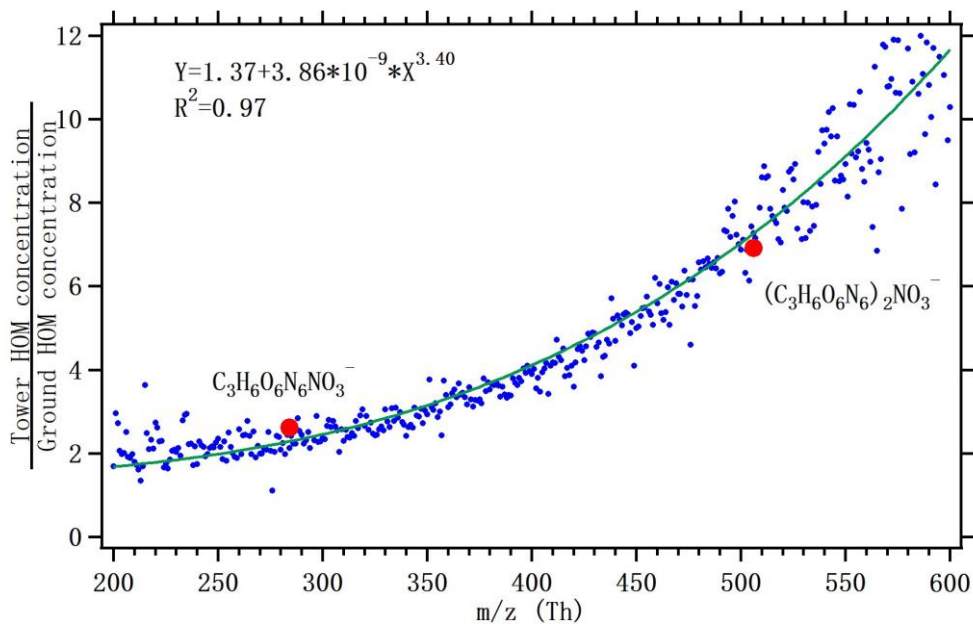
138 flow of 7 lpm (liter per minute), and then centered to an ion reaction tube surrounded
139 by sheath flow (filtered air, 35 lpm). Meanwhile, the nitrate ions carried by the sheath
140 gas, which were generated by exposing the nitric acid (HNO₃) to soft x-ray radiation,
141 were guided into the sample gas by an electrical field at ambient pressure (~100 ms
142 reaction time). Neutral molecules (M) in the sample air were ionized by either
143 clustering with charged nitrate/nitric acid ((HNO₃)_{n=0-2}·NO₃⁻) to form (M)·NO₃⁻ cluster
144 ions, or losing a proton to the charging ions to form deprotonated ions (e.g.,
145 H₂SO₄+NO₃⁻→HSO₄⁻+HNO₃). The ions then entered the APi part, which was a three-
146 stage vacuum chamber, through a pinhole. In the APi, two quadrupoles and stack of ion
147 lenses guide the ions into the TOF mass spectrometer, where ions were separated based
148 on their mass-to-charge (*m/z*) ratios. A more detailed description of this instrument has
149 been given by Junninen et al. (2010) and Jokinen et al. (2012). Mass spectra obtained
150 from the instrument were analyzed using the ‘tofTools’ program described in Junninen
151 et al. (2010). Determination of the concentration of a measured molecule M was based
152 on the following equation:

$$153 \quad [M] = \frac{\sum M}{\sum \text{reagent ion count rates}} \times C \quad (1)$$

154 where the sum of ion count rates was an inclusion of all detected ions relating to
155 compound *M*, whether deprotonated or in clusters with reagent ions, and the sum of
156 reagent ion count rates is the total signal of the charged nitric acid ions. *C* was the
157 calibration coefficient, which was assigned the same value for all detected compounds.
158 This assignment is only valid for compounds that cluster with the reagent ions at the
159 collision limit, such as H₂SO₄ (Viggiano et al., 1997) and have equal collision rates.
160 The collision rates of nitrate ions with H₂SO₄ and with HOMs are expected to be very
161 close (Ehn et al., 2014). Here, a calibration coefficient of 1 × 10¹⁰ molec cm⁻³, estimated
162 from previous calibrations with similar settings using sulfuric acid and theoretical
163 constraints (Ehn et al., 2014), with an uncertainty of at least -50%/+100%, was used in
164 calculating the HOM concentrations for both instruments. Ultimately, the absolute
165 HOM concentrations in this work are of secondary importance, as we focus on the

166 relative comparison of HOM concentrations measured at different heights. However,
167 the comparability of the two CI-APi-TOF instruments is of great importance, and
168 results cannot be allowed to vary e.g. as a result of inevitable differences in the mass-
169 dependent transmission efficiency (TE). To this end, instead of directly evaluating the
170 TE of each instrument, a “relative” TE of the two CI-APi-TOFs was used for data
171 correction: we selected a time period at noon-time on September 9 with well-mixed
172 boundary layer condition, identified with the clear and sunny weather and
173 homogeneous vertical distribution of monoterpene and other trace gases, and assumed
174 the HOM concentrations at the two heights to be the same. Thus, the relative TE was
175 obtained from the concentration ratio between the two CI-APi-TOFs at each m/z (Figure
176 1). Weaker correlation was obtained in the 200-250 Th mass range, but in the mass
177 range where most of the HOMs were located (290-600 Th) there is very little scatter
178 around the fitted curve, clearly suggesting that observed differences in the two
179 instruments responses were mainly due to differences in TE. Additionally, an inter-
180 comparison between the two instruments with a permeation tube containing
181 trinitrotriazinane ($C_3H_6N_6O_6$) was conducted in the field right after the campaign. The
182 results showed good agreements with the relative TE, lending confidence to the method
183 used here. Finally, it should be noted that the difference in TE between the two
184 instruments was larger than one would normally expect, since the tower CI-APi-TOF
185 had been tuned for higher sensitivity at the largest masses (at the expense of
186 transmission at the lower masses).

187



188

189 Figure 2 The relative TE curve between the two CI-API-TOF mass spectrometers. Inter-comparison
190 results using a permeation tube containing trinitrotriazinane (C₃H₆N₆O₆) are shown in red circles.

191

192 In comparison to the direct determination of TE (Heinritzi et al., 2016), this method
193 increases the uncertainty in the quantification of HOM concentrations. However, as
194 mentioned, a more accurate knowledge of the exact HOM concentrations would not
195 influence the main findings of this study.

196

197 The MT, trace gases, and meteorological parameters were continuously monitored at
198 the different heights (4.2 m, 8.4 m, 16.8 m, 33.6 m, 50.4 m, 67.2 m, 101m, and 125 m)
199 on a 126 m mast ~100 m away from the location of the CI-API-TOFs. The data at 4.2
200 m and 33.6 m were used in this study to represent the concentrations at near ground and
201 tower level, respectively. Ambient MT concentration was measured every third hour
202 using a proton transfer reaction mass spectrometer with a lower detection limit of 1
203 pptv (PTR-MS, Ionicon Analytik GmbH; Taipale et al., 2008). The O₃ concentration
204 was measured with an UV light absorption analyzer that had a lower detection limit of
205 1 ppbv (TEI model 49C, Thermo Fisher Scientific, USA). The NO_x measurement was
206 conducted using a chemiluminescence analyzer (TEI model 42C TL, Thermo Fisher

207 Scientific, USA). The lower detection limit of the NO_x analyzer is 100 pptv. The CO₂
208 measurement was performed using an infrared detection system (LI-840, LiCor
209 Biosciences, Lincoln, NE, USA). The aerosol number concentration size distributions
210 were obtained with a twin differential mobility particle sizer (twin-DMPS) for the size
211 range from 3-1000 nm (Aalto et al., 2001) at 8 m height above ground, and was used to
212 calculate condensation sink (CS) based on the method from Kulmala et al. (2001). Air
213 temperature was measured with PT-100 resistance thermometers. Air relative humidity
214 (RH) was measured with RH sensors (Rotronic Hygromet model MP102H with
215 Hygroclip HC2-S3, Rotronic AG, Switzerland). Global radiation (solar radiation in
216 wavelength range of 0.3-4.8 μm) was obtained with a Pyranometer (Reemann TP3,
217 Astrodata, Estonia) above the canopy top at 18 m. All the data presented are at 10 min
218 averaging intervals, except for the MT (in 1-hour averaging interval).

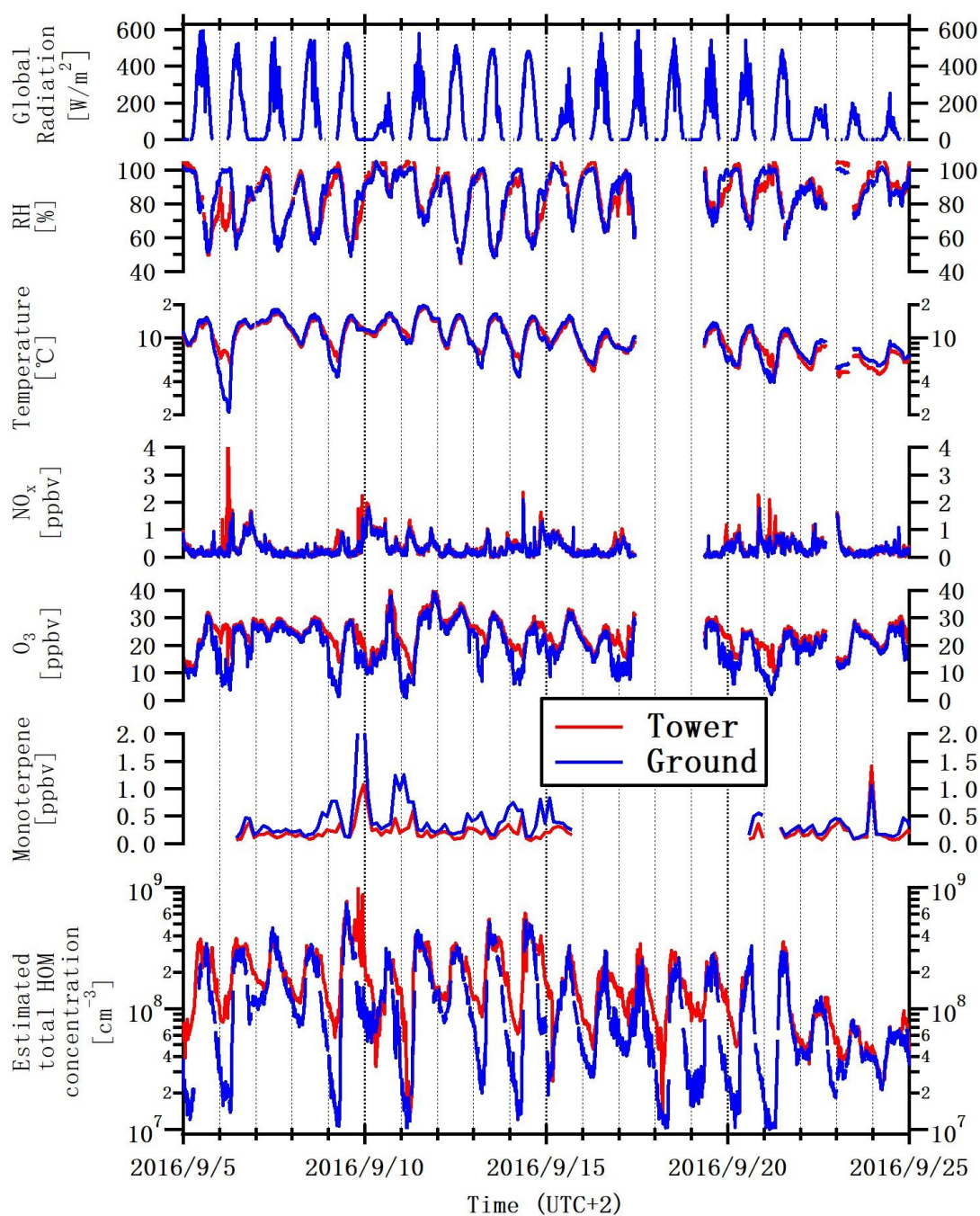
219

220 **Results and discussion**

221 **1.3 Data overview**

222 The Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget
223 (IBAIRN) campaign was conducted from September 1 to 25, 2016. After data quality
224 checks, only the measurements collected after September 5 were used. Figure 2 shows
225 the overall time series of the meteorological parameters measured at ground and tower
226 levels, including the temperature, RH, global radiation, concentrations of trace gases,
227 MT, and total HOMs. The weather was generally sunny and clear during the campaign
228 except for a few cloudy (September 10, 15, and 22-23) and drizzling (September 24
229 and 25) days. The mean air temperature and RH observed at ground level were $10.8 \pm$
230 3.3 °C and 87 ± 13 % (1σ standard deviation), and at the tower level were 10.5 ± 3.0 °C
231 and 88 ± 14 %, respectively. The O₃ concentrations measured at ground and tower levels
232 were 21 ± 8 ppbv and 25 ± 6 ppbv, respectively. The air temperature, RH and O₃
233 measured at the two heights were close to each other during daytime. The NO_x

234 concentrations were quite low throughout the campaign, the mean NO_x concentrations
 235 were mostly around the reported detection limit at 0.4 ± 0.4 ppbv (ground) and $0.4 \pm$
 236 0.5 ppbv (tower), yet showed an overall good agreement between the measurements at
 237 the different heights. The MT concentrations at ground level (0.38 ± 0.34 ppbv on
 238 average) were generally higher than that above the canopy level (0.20 ± 0.16 ppbv).
 239



240

241 Figure 3 The overall time series of the measured trace gases, meteorological parameters and estimated

242 total HOM concentrations at the ground (blue) and tower (red) levels.

243

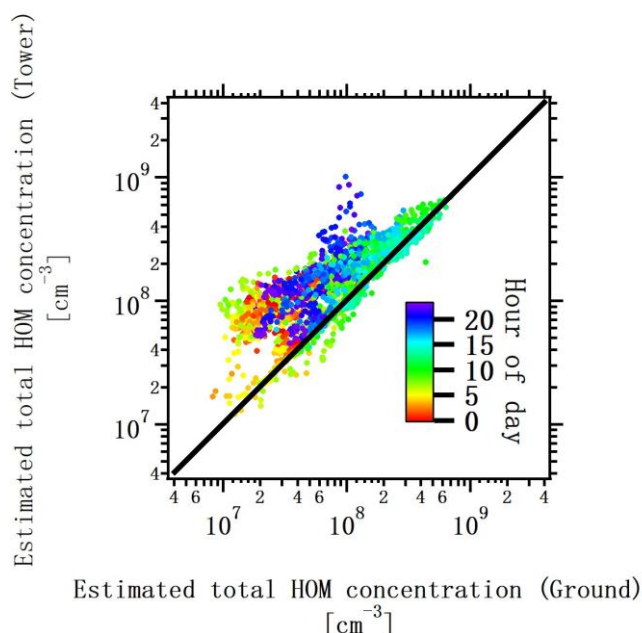
244 The **estimated** total HOM concentration is representative for the overall concentration
245 level of HOMs, and is defined as the sum of the detected signals between ions from m/z
246 200 to 600 after removing the identified background peaks. The gaps in the ground
247 **estimated** total HOM data were due to automatic zero-check. During the campaign, a
248 significant difference was found in the **estimated** total HOM concentrations below and
249 above the canopy (mean and median concentrations of $1.1 \pm 1.7 \times 10^8 \text{ cm}^{-3}$ and $7.6 \times$
250 10^7 cm^{-3} at ground level, $1.7 \pm 1.3 \times 10^8 \text{ cm}^{-3}$ and $1.3 \times 10^8 \text{ cm}^{-3}$ at tower level). The
251 causes of these differences (**$\sim 55\%$ in mean and $\sim 71\%$ in median**) frame the upcoming
252 discussion.

253

254 4.2 Inter-comparison of **estimated** total HOM concentrations

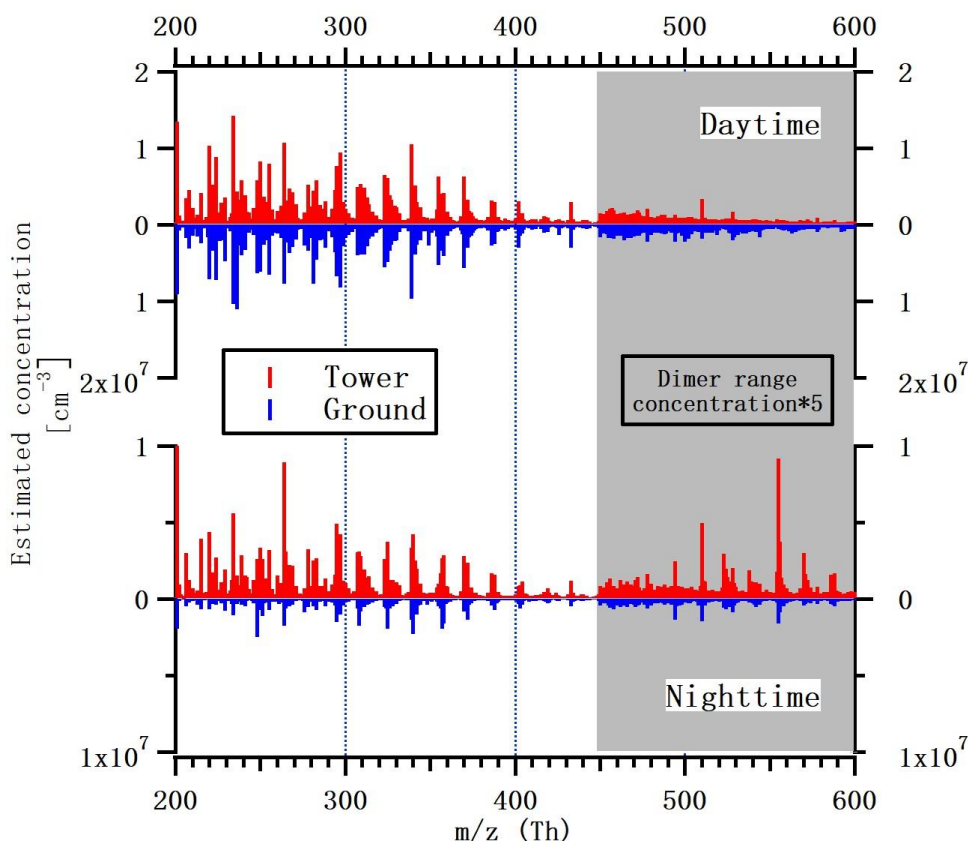
255 The **estimated** total HOM concentrations at the two heights were not different during
256 the day (**mean $\pm 1\sigma$ standard deviation and median concentrations of $4.1 \pm 2.3 \times 10^8 \text{ cm}^{-3}$**
257 **3 and $3.6 \times 10^8 \text{ cm}^{-3}$ at ground level, $4.3 \pm 2.6 \times 10^8 \text{ cm}^{-3}$ and $4.0 \times 10^8 \text{ cm}^{-3}$ at tower**
258 **level), which validates the use of only one day of data for scaling the TE of the ground**
259 **CI-APi-TOF to match the HOM signals. The good daytime agreement throughout the**
260 **campaign period also verifies that the response of each instrument stayed stable.**
261 **Contrary to the daytime results, the **estimated** total HOM concentration at ground level**
262 **usually diverged from the tower measurement in the nocturnal boundary layer. The**
263 **concentration below the canopy became even lower when temperature inversions were**
264 **observed, accompanied by a decreasing ground-level O_3 and increasing MT**
265 **concentrations. Figure 3 shows the correlation between the **estimated** total HOM**
266 **concentrations observed at two heights. Herein, good agreement could be found for the**
267 **group of points representing the concentrations around noontime ($R^2 = 0.89$). The**
268 **points indicating the nighttime **estimated** total HOM concentrations were scattered (R^2**

269 = 0.28), and the ground concentrations were found to be much lower than the tower
270 ones.
271



272
273 Figure 4 Correlation between ground (x-axis) and tower (y-axis) measurements of the **estimated** total
274 HOM concentrations. The black line denotes the 1:1 ratio. Color code indicates the sampling time of
275 HOMs.
276
277 Figure 4 shows the mean **mass** spectra (in unit mass resolution, UMR, **for** m/z 200 –
278 600) obtained from the ground and tower. It is worth mentioning that there might be
279 some signals not attributable to HOMs in the plotted spectra, but only in little proportion.
280 Only selected periods (09:00-15:00 for daytime and 21:00-03:00 for nighttime, local
281 winter time (UTC +2)) are included in the averaging period to eliminate the effect of
282 sunrise and sunset periods. During daytime, a good agreement ($R^2 = 0.87$) was obtained
283 from the mass-by-mass comparison using the UMR concentrations extracted from
284 daytime mean spectra, suggesting a uniform composition distribution in the daytime
285 boundary layer condition. During nighttime, the mean concentrations of all HOM
286 molecules in the ground mean spectra were much lower than the tower spectra. The

287 HOM concentrations shown in the ground and tower mean spectra were also less
 288 correlated. Therefore, a logical outcome is that the conditions below and above the
 289 canopy are experiencing different turbulent mixing strength **and/or** source-sink regimes
 290 during night.
 291



292
 293 Figure 5 Mean mass spectra with the averaging periods of daytime (09:00-15:00) and nighttime (21:00-
 294 03:00) at ground and tower levels.

295 4.3 Influence of nocturnal boundary layer dynamics and micrometeorological 296 processes

297 The nighttime HOMs at ground level are **likely** influenced by transport processes below
 298 the canopy, since the **estimated** total HOM concentrations were found much lower in
 299 the nights when temperature inversions were observed. To further investigate the
 300 potential impact **of** such micrometeorological phenomena on ground HOMs, **for** the
 301 nights during the campaign **without** precipitation **or** instrument failure, were selected

302 (12 nights in total) and categorized into 2 types based on the **occurrence** of temperature
303 inversions: 1) the “non-inversion night” type included 6 nights when no temperature
304 inversion was recorded; 2) the “inversion night” type **category consisted of** 6 nights that
305 had encountered temperature inversions, and the ground temperatures were generally
306 ~1 °C lower **than** tower temperatures during these nights.

307

308 **4.3.1 Statistics of the “non-inversion night” and “inversion night” types**

309 Table 1 shows the overall statistics including the mean, median, 25% percentile and 75%
310 percentile values of the temperatures, O₃, NO_x, MT and **estimated** total HOM
311 concentrations for the “non-inversion night” and “inversion night” types. In the non-
312 inversion nights, the air below and above the canopy **was** relatively well-mixed. The
313 mean and median concentrations of the ground O₃ (**21 ± 8** ppbv and **22** ppbv) were
314 close to the tower values (**25 ± 6** ppbv and **24** ppbv). The slight difference might be
315 attributed to the higher VOC emissions (**Rantala et al., 2014**) and larger sink near
316 ground level. In contrast, during the inversion nights, the mean **estimated** total HOM
317 concentration and O₃ at ground level were generally much lower, only ~33% and ~69%
318 of the tower concentrations, respectively. Instead, the mean and median ground MT
319 concentration (**0.70 ± 0.28** ppbv and **0.70** ppbv) were ~3 times higher than the tower
320 ones (**0.24 ± 0.04** ppbv and **0.23** ppbv), respectively. The measured NO_x levels were
321 similar in both **categories** and heights, though the ambient concentrations were close to
322 the detection limit and therefore small differences might not be observable.

323

324 **4.3.2 Case study**

325 Two individual nights representing the “non-inversion night” and “inversion night”
326 types were selected and further compared. Figure 5a shows the time series of the
327 meteorological parameters, trace gases and HOMs measured at ground and tower

328 levels of one selected night of “non-inversion night” type (September 11-12, from 21:00
329 to 03:00). A number of measures can be used to assess the local atmospheric stability
330 conditions at a given layer. These measures are commonly based on either the Obukhov
331 length and its associated atmospheric stability parameter or a Richardson number (flux-
332 based, gradient-based, or bulk). Because of its simplicity and the availability of high
333 resolution mean air temperature profiles, the bulk Richardson number (Ri) was used
334 here (Mahrt et al., 2001; Mammarella et al., 2007; Vickers et al., 2012; Alekseychik et
335 al., 2013). It is calculated using:

$$336 \quad Ri = \frac{g\Delta\bar{\theta}\Delta z}{\bar{\theta}(\bar{u})^2} \quad (2)$$

337 where g is the gravitational acceleration, $\Delta\bar{\theta}$ and Δz are the mean potential
338 temperature (10 min averaging interval, same as measurement data) and height
339 difference between the ground and tower levels, respectively, $\bar{\theta}$ and \bar{u} are the mean
340 potential temperature and mean wind velocity at tower level, respectively. During the
341 selected “non-inversion” night, Ri was generally positive but close to 0 (shown in
342 Figure 5a), indicating a weakly stable and relatively well-mixed (i.e. $\Delta\bar{\theta} \rightarrow 0$)
343 condition (Mahrt, 1998; Mammarella et al., 2007). This was also confirmed using the
344 well correlated ground and tower MT and trace gases concentrations.

345

346 **Table 1** Summary of the "Non-inversion night" and "Inversion night" types.

Type		Non-inversion night					Inversion night				
Date		September 6, 7, 9, 11, 15, 16, 21*					September 5, 8, 10, 12, 13, 14, 19**				
Parameters		Temperature [°C]	O ₃ [ppbv]	NO _x [ppbv]	MT [ppbv]	Estimated total HOM [10 ⁸ cm ⁻³]	Temperature [°C]	O ₃ [ppbv]	NO _x [ppbv]	MT [ppbv]	Estimated total HOM [10 ⁸ cm ⁻³]
Tower	Mean ± 1σ standard deviation	10.2 ± 2.6	25 ± 6	0.5 ± 0.5	0.31 ± 0.31	2.9 ± 1.9	9.5 ± 1.7	24 ± 2	0.4 ± 0.3	0.24 ± 0.04	2.4 ± 0.8
	Median	10.9	24	0.4	0.17	2.8	9.2	23	0.3	0.23	2.3
	25% / 75% percentile	7.9 / 12.4	21 / 27	0.2 / 0.7	0.15 / 0.24	2.2 / 3.2	8.1 / 10.9	22 / 25	0.2 / 0.5	0.21 / 0.26	1.8 / 2.8
Ground	Mean ± 1σ standard deviation	10.6 ± 2.7	21 ± 8	0.4 ± 0.4	0.52 ± 0.74	1.6 ± 0.6	8.3 ± 2.2	16 ± 6	0.3 ± 0.2	0.70 ± 0.28	0.8 ± 0.4
	Median	11.5	22	0.3	0.22	1.7	8.5	17	0.3	0.70	0.7
	25% / 75% percentile	8.1 / 12.8	15 / 26	0.2 / 0.5	0.21 / 0.31	0.9 / 3.2	6.6 / 9.9	11 / 22	0.2 / 0.4	0.46 / 0.82	0.5 / 1.2

347 *MT data not available on September 5 and 19.

348 **MT data not available on September 15 and 16

Selected HOM molecules representing the major HOM types (and formation pathways) were summed up and categorized into 4 groups, as shown in Table 2. Each pathway might be influenced differently by boundary layer dynamics and micrometeorological processes. In this study, OH-initiated HOMs were assumed negligible due to the very low OH level in the nocturnal boundary layer.

Table 2 Compositions of selected HOM molecules and their main oxidants (Yan et al., 2016).

	Molecule compositions	Main oxidants	Main terminators
CHO_{monomer}	C ₁₀ H ₁₄ O ₇ , C ₁₀ H ₁₄ O ₉	O ₃	Self-terminate or RO ₂
CHON_{monomer}	C ₁₀ H ₁₅ O ₉ N, C ₁₀ H ₁₅ O ₁₁ N	O ₃ or NO ₃	NO or Self-terminate/RO ₂
CHO_{dimer}	C ₁₉ H ₂₈ O ₁₁ , C ₂₀ H ₃₀ O ₁₄	O ₃	RO ₂
CHON_{dimer}	C ₂₀ H ₃₂ O ₁₂ N ₂ , C ₂₀ H ₃₁ O ₁₃ N	NO ₃	RO ₂

All the HOM groups in Figure 5a show stable patterns, and good agreement is observed between the ground and tower measurements in the first half of the night. Variations were observed when air mass change occurred at around 01:00, as indicated by the drop of NO_x concentration and CS, and wind shift (not shown here). However, the HOM groups were still well correlated with each other, suggesting the unchanged well-mixed condition in the non-inversion night.

Figure 5b shows the time series of the trace gases, MT, and HOM groups **of both ground and tower measurements** during an “inversion night” case (September 8-9, from 21:00 to 03:00). *Ri* was generally higher during this night, and increased from ~0.03 (indicating weakly stable condition, Mammarella et al., 2007), at around midnight, to a maximum of ~1.13 (indicating very stable condition) in the remaining night period. Roughly, *Ri values* in excess of unity indicate that stably stratified conditions appreciably diminish the inverse turbulent Prandtl number (*Pr*) and the efficiency of turbulence to mix heat when compared to momentum (Katul et al., 2014). The

parameters measured at tower level were not significantly affected by strong Ri fluctuations throughout the night, in contrast, significant variations were observed at ground level.

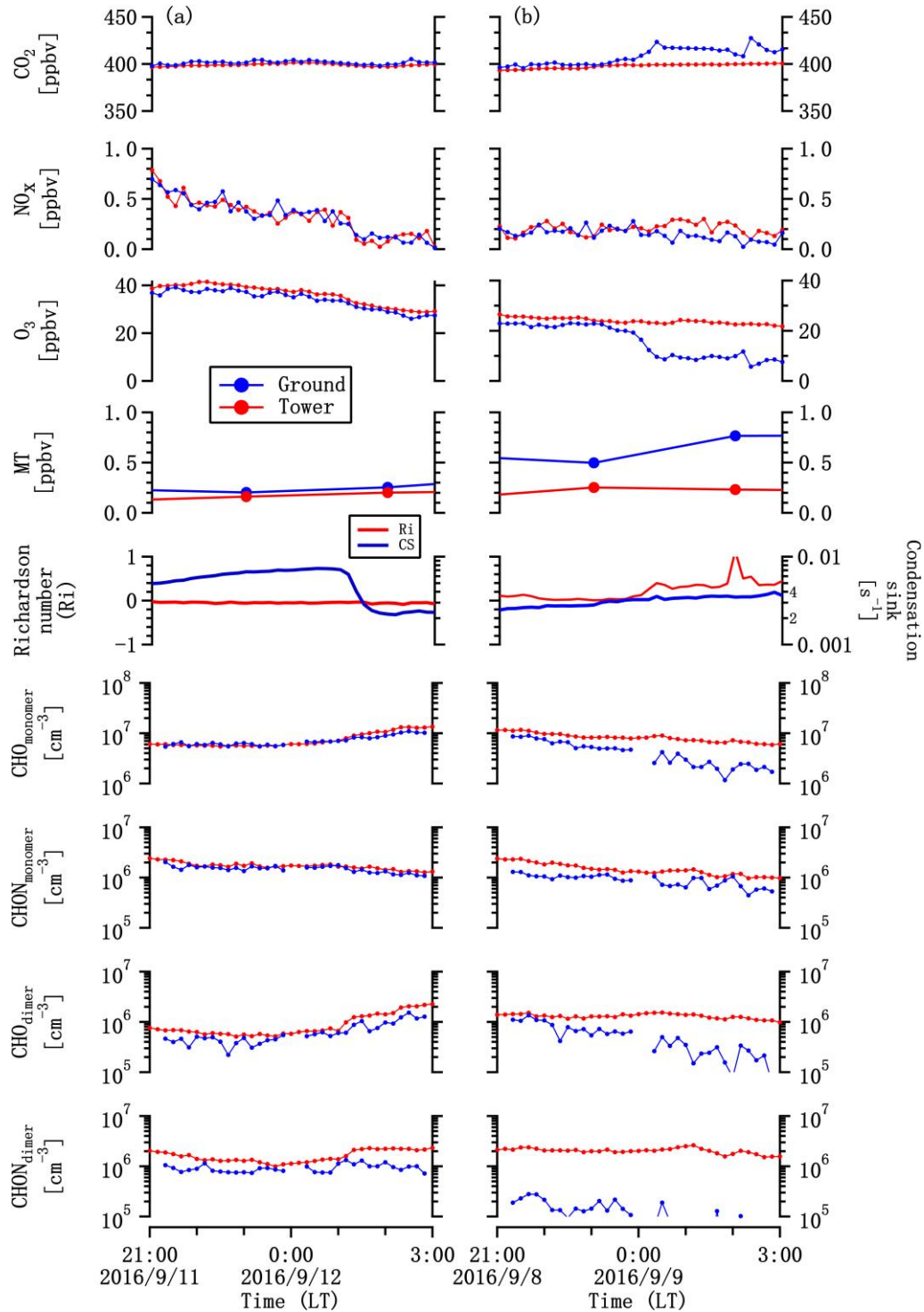


Figure 6 (a) Time series of ground and tower concentrations of CO₂, NO_x, O₃, MT, and selected HOM groups in the selected “non-inversion night” (September 11), and (b) “inversion night” (September 8).

Ri is calculated with the meteorology data of ground and tower levels. CS is determined based on the aerosol data measured at 8 m above ground level.

The ground O₃ concentration experienced a rapid decrease at midnight. In about an hour (from 23:30-00:30), ground O₃ concentration dropped by more than half (from 20 ppbv to 9 ppbv), and CO₂ concentration increased as well (from 404 ppbv to 423 ppbv). To the contrary, the MT concentration at ground level was almost doubled (from 0.49 ppbv to 0.80 ppbv) during the same period. Theoretically, the enhancement of HOM precursor and decrease of oxidant would compensate each other if the sink remained the same, and the ground HOM concentrations should also keep constant. However, all the HOM groups showed significant decrease **after** midnight. In particular, the concentration of the CHO_{monomer} group dropped ~80%, from $8.6 \times 10^6 \text{ cm}^{-3}$ to $1.7 \times 10^6 \text{ cm}^{-3}$, and the concentration of the CHO_{dimer} group decreased from $1.5 \times 10^6 \text{ cm}^{-3}$ to $\sim 1.0 \times 10^5 \text{ cm}^{-3}$. The concentrations of the CHON_{monomer} and CHON_{dimer} groups also experienced large declines (~34% and ~50%, respectively), in the latter half of the night. At 03:00, the CHON_{dimer} concentration was already below the detection limit ($1 \times 10^4 \text{ cm}^{-3}$). Therefore, the much lower ground HOM concentrations might not be totally explained by the change of HOM production, but also **due to** some other processes **such as additional losses**.

A previous study by Alekseychik et al. (2013) **at SMEAR II station** showed that nocturnal decoupled air layers were frequently (with a fraction of 18.6% based on a long-term dataset) observed under high *Ri* conditions in the boreal forest. The decoupled layer could strongly influence the ground O₃, MT, and CO₂ concentrations (Rannik et al., 2009, 2012; Alekseychik et al., 2013; Chen et al., 2018), and could also explain the occurrence of the strong temperature inversion during the inversion nights. To explore the possible mechanism resulting in significantly different O₃, MT and HOM concentrations **below the canopy**, the mean continuity equation for high Reynolds number flows within the canopy is formulated as (e.g. Katul et al. 2006):

$$\frac{\partial \bar{C}}{\partial t} + \bar{U} \frac{\partial \bar{C}}{\partial x} + \bar{W} \frac{\partial \bar{C}}{\partial z} = -S - \frac{\partial \overline{w'c'}}{\partial z} - \frac{\partial \overline{u'c'}}{\partial x} \quad (3)$$

$$N_1 + N_2 + N_3 = N_4 + N_5 + N_6 \quad (4)$$

where t is time, x and z are the longitudinal and vertical directions, respectively, C is the scalar concentration, U and W are the longitudinal and vertical velocity components, $\overline{w'c'}$ and $\overline{u'c'}$ are the turbulent scalar fluxes in the vertical and horizontal, respectively, and S represents the net sources or sinks (physical, chemical, and biological) of C , and overline represents time averaging over turbulent scales. The 6 terms in this equation represent the following (left to right): local rate of change (= N_1), horizontal advection by the mean velocity (= N_2), vertical advection by the mean velocity (= N_3), net sources or sinks (= N_4), net vertical transport by the vertical turbulent flux gradient (= N_5), net horizontal transport by the horizontal turbulent flux gradient (= N_6). Generally, $|N_6| \ll |N_5|$, and is hereafter ignored in the discussion.

During the non-inversion night, the ground O_3 could be replenished either by vertical turbulent transport (N_5), mean vertical advection from upper boundary layer (N_3), or horizontal advection below the canopy (N_2) (as shown in Figure 6). However, for highly stratified flows, N_5 becomes small, as the efficiency of turbulence to transport O_3 to layers near the ground becomes weak (Katul et al., 2014). Vertical and horizontal advection were also small within such a stable layer, and the reduced mean velocity would result in smaller contributions from N_2 and N_3 . Note that these advective terms tend to be opposite in sign by the virtue of the mean fluid continuity equation (Katul et al., 2006). Instead, the sink of O_3 (N_4) was stronger because of the increasing loss due to a higher surface area-to-volume density (S/V) in this shallow decoupled layer. Under this circumstance, the ground O_3 concentration dramatically decreased when the air layer was forming, and eventually reached a much lower concentration. The decoupled layer also affected MT and CO_2 below the canopy in the inversion night, but resulted in concentration increases as opposed to O_3 . The weakened vertical turbulence (N_5) tended to retain the emissions from ground and understory vegetation within the layer,

though N_4 also increased. In general, the increased CO_2 (primary source from the ground) and MT (primary source from the canopy) at ground level are good indicators for the extent of the mixing in the shallow decoupled layer. At the same time, the strong decrease of O_3 shows how the sinks in this layer are no longer balanced by a large flux of O_3 from upper layers. However, the stabilization of ground-level O_3 concentrations at non-zero values after the initial fast decrease suggests that a small amount of inflow, either via N_3 or N_5 , is still taking place.

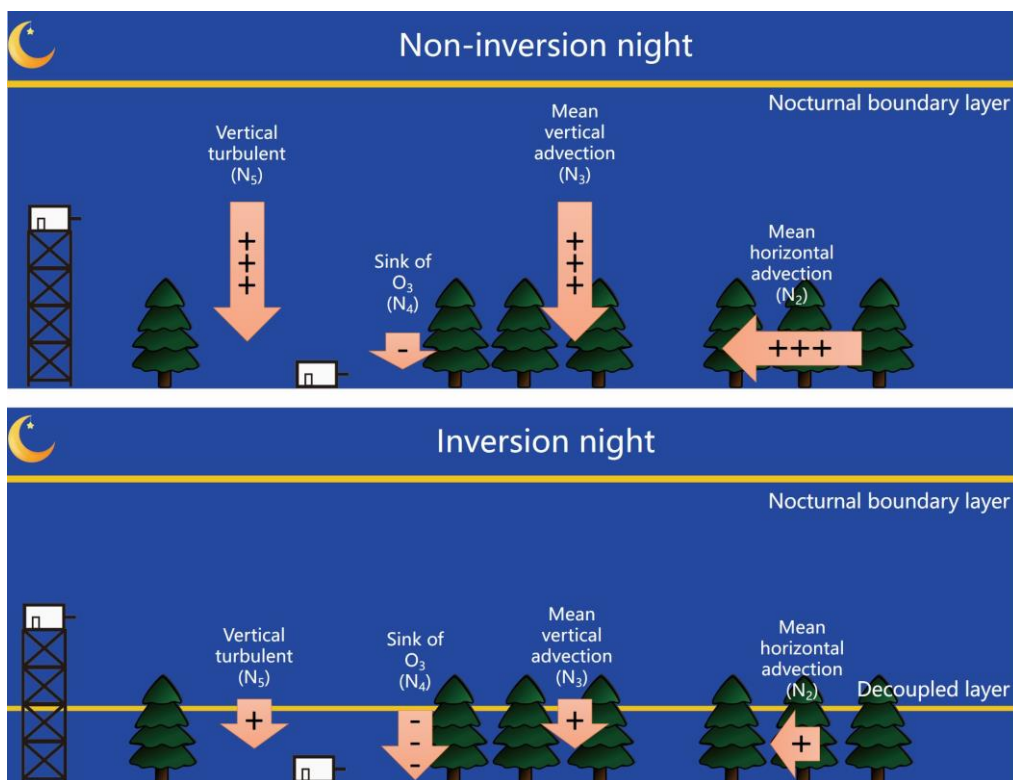


Figure 6 Schematic figure showing how vertical mixing, vertical advection, and horizontal advection influence ground O_3 concentrations differently in non-inversion night and inversion night in boreal forest.

Therefore, the differences between the ground and tower measurements were due to the joint effects of: (i) decoupling between the stably stratified near-ground layer and the canopy top, and the consequent formation of a shallow layer, (ii) weakening of advective and turbulent flux transport terms thereby inhibiting mass exchange between the ground decoupled layer and the remaining nocturnal boundary layer, and (iii)

increased surface area to volume within the decoupled layer thereby enhancing N_4 .

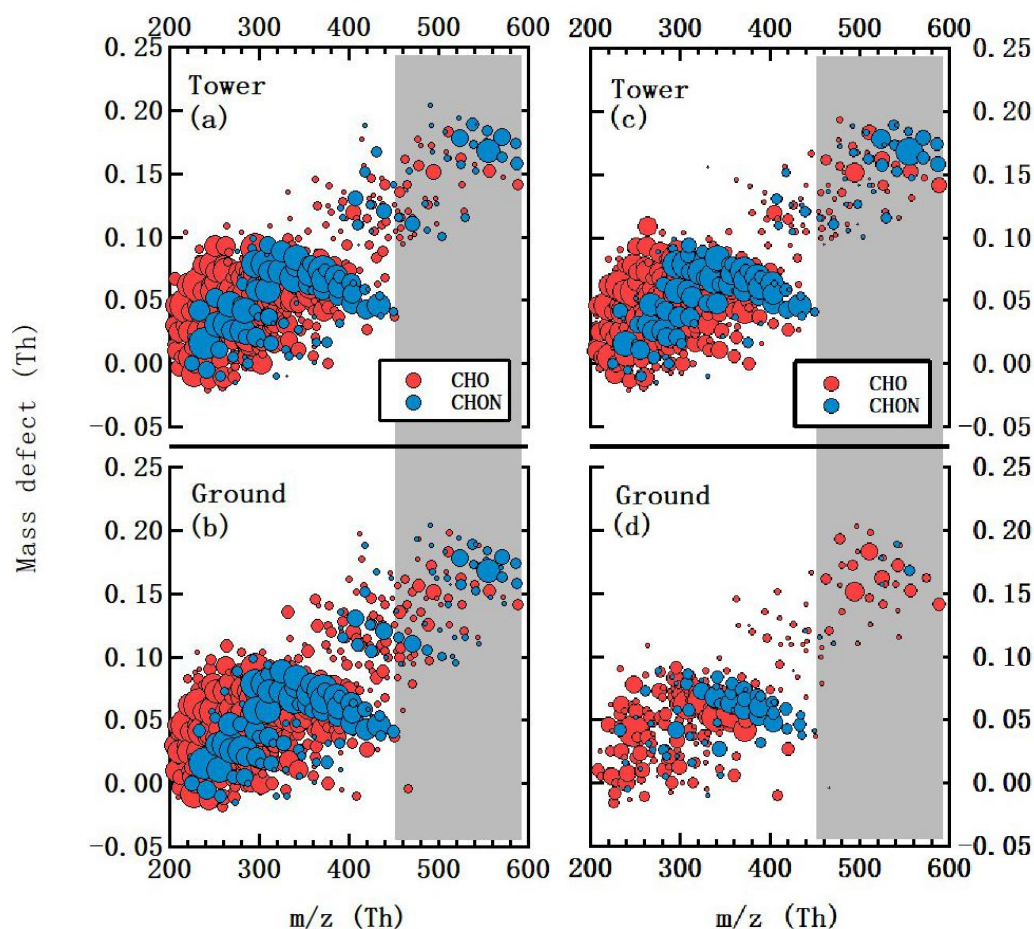


Figure 7 Mass defect (MD) plots of the selected “non-inversion night” case (September 11), at (a) tower and (b) ground levels; and “inversion night” case (September 8), at (c) tower and (d) ground levels. The grey shade area denotes the dimer range (m/z 450-600).

Examination of the selected HOM molecules was useful and efficient to assess the changes in HOMs, however, **such an analysis might only indicate the** major formation pathways. Hence, it was also worthwhile to have a holistic view **of the entire** mass spectra and all the detected HOMs. The mass defect (MD) plot, with the exact masses of the compounds on the x-axis, the deviation from the integer mass on the y-axis, the compounds plotted in circles and the areas scaled by concentrations, shows the abundance and chemical speciation of all the detected HOMs in the spectra. Figure 7a and 7b are MD plots showing the mean spectra of the selected non-inversion night

(September 11) at tower and ground levels. Without the formation of a decoupled layer, nearly identical composition distribution of HOMs were observed. In contrast, during the inversion night (September 8, Figure 7c and 7d), large differences could be found between the two measurement heights. Moreover, a significant fraction of the ground HOMs disappeared on the inversion night, and the concentrations of the remaining HOMs were also lower, confirming the aforementioned results obtained with the selected HOM groups.

1.4 Study limitations

Several limitations still exist in this study. From the measurement side, one major concern was the comparability between our two CI-APi-TOF mass spectrometers. In the worst case, our conclusion might be biased if instrument responses changed due to some parameter that correlated with the observed inversions. The main parameters in this case would be ambient temperature and RH. As both instruments were located in temperature-controlled containers and the sample flow was mixed 1:2 with dry sheath air in the CI-APi-TOF drift tube, neither of these were expected to yield such large changes. However, for confirmation, we compared the detailed spectral evolution during days and nights of the study. Figure 8 shows an example of hourly changes of the ratios between tower and ground HOMs, over a 24h period without nighttime temperature inversion (September 11). During this period, ambient temperatures changed from 19.1 °C (12:00 LT) to 8.8 °C (07:00 LT) at ground level, and from 17.9 °C to 8.1 °C at tower level. Ambient RHs also increased from 72 % to 96 % at ground level, and from 74 % to 98 % at tower level. While some scatter is visible in the 200-300 Th range during some parts of the night, good agreement was observed between the two instruments throughout the night, despite large variability in temperatures and RHs.

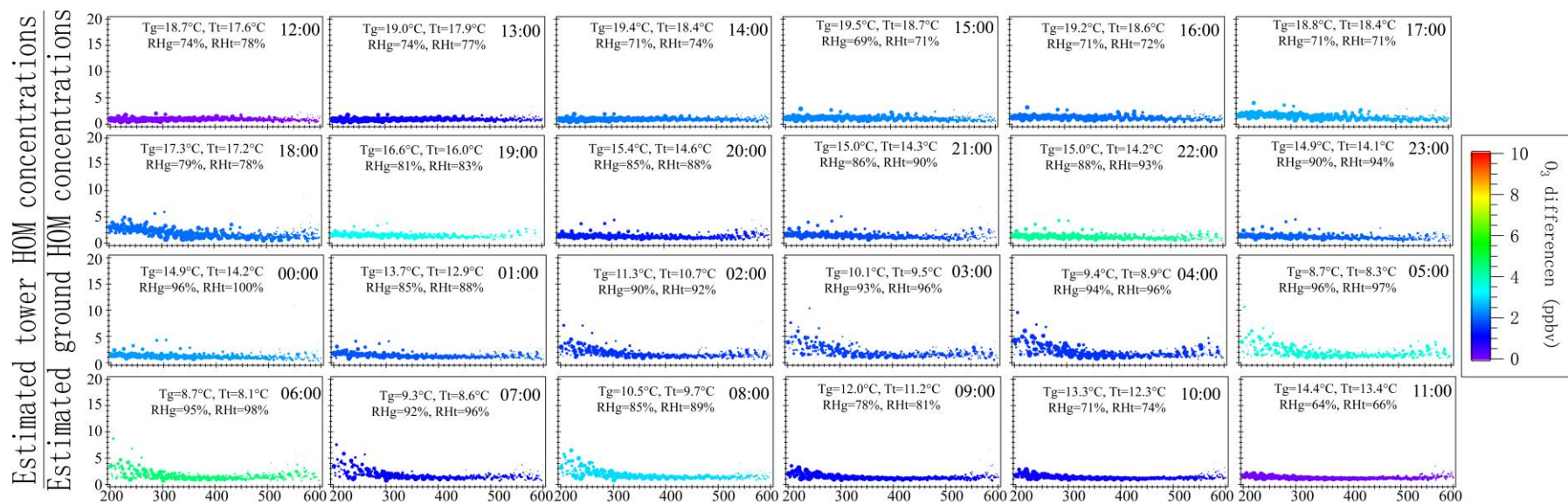


Figure 8 Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 11, 12:00 to September 12, 11:00 (non-inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3,tower} - O_{3,ground}$). Hourly ambient temperatures at ground (Tg) and tower (Tt) levels, and RH at ground (RHg) and tower (RHt) levels are shown in each subplot.

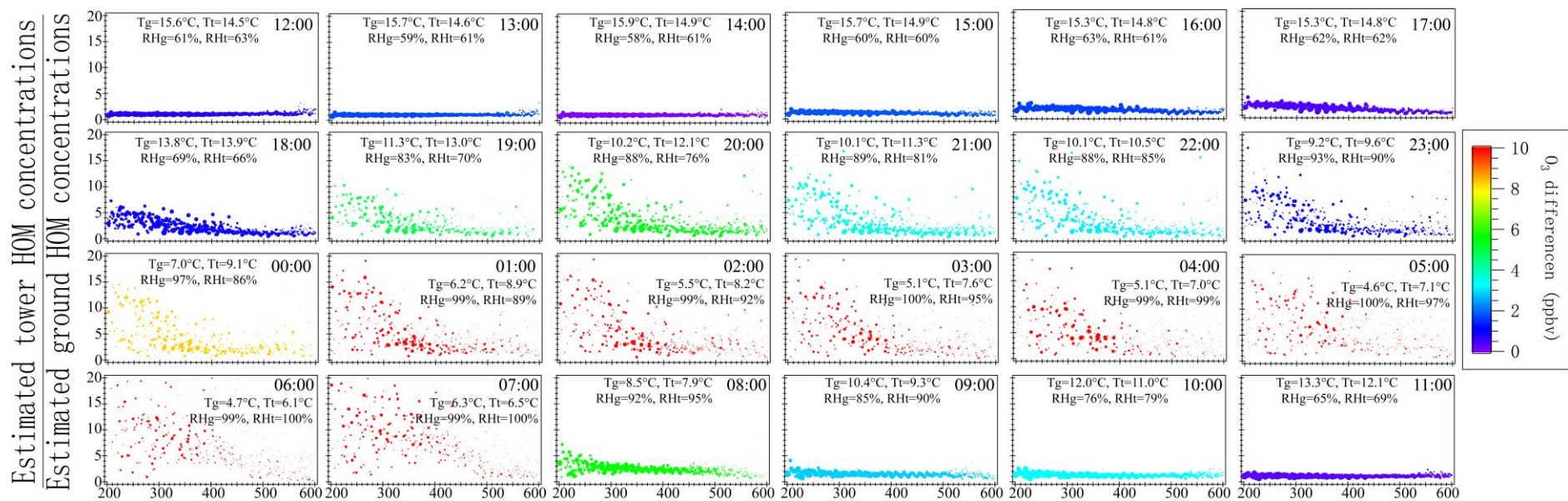


Figure 9 Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 8, 12:00 to September 9, 11:00 (inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3_{tower}} - O_{3_{ground}}$). Hourly ambient temperatures at ground (Tg) and tower (Tt) levels, and RH at ground (RHg) and tower (RHt) levels are shown in each subplot.

318 In contrast, during a 24h period with nighttime temperature inversion (September 8,
319 shown in Figure 9), the ratios agreed well only during daytime (from 12:00 to 17:00,
320 and 09:00-11:00 on the next day). Between these periods, temperature and RH were
321 most of the time in the same range as on September 11 (when no strong deviations were
322 observed), but now the HOM behavior changed dramatically between the two heights.
323 The ratios increased from ~ 1 (during daytime) up to ~ 20 at 07:00 for some of the
324 measured molecules.

325

326 Figures 8 and 9 clearly imply that the large differences between ground and tower HOM
327 concentrations were driven by temperature inversions and consequent changes in the
328 composition of the air in the two detached layers. Large changes in HOMs were
329 observed only when the ground temperature was lower than the tower temperature and
330 when the ozone concentration at ground level was several ppb lower. Absolute
331 temperatures or RHs at the two heights were not able to explain the changes. As a
332 concrete example, good agreement was observed at 07:00, September 12, while
333 ambient temperatures were low (ground and tower temperatures were 9.3 °C and 8.6 °C,
334 respectively) and RHs were high (ground and tower RHs were 92 % and 96 %,
335 respectively), but large deviations were found at 20:00, September 8, when higher
336 temperatures (ground and tower temperatures were 10.2 °C and 12.1 °C, respectively)
337 and lower RHs (ground and tower RHs were 88 % and 76 %, respectively) were
338 observed. In other words, neither low temperatures nor high RHs caused large changes
339 to our instruments. Instead, the large discrepancies between the two CI-API-TOFs were
340 only observed when other key parameters (like ozone) were found to deviate
341 considerably between the two heights.

342

343 From micrometeorology side, the contribution from the potential micrometeorological
344 processes in the layer between 1.5 m and 4.2 m (between the sampling heights of the
345 ground HOMs and other parameters) could not be estimated with the current experiment

346 design (i.e., only two measurement heights). Similarly, the influence from horizontal
347 advection could not be entirely ruled out as a contributor to the reduced ground-level
348 HOM concentrations (and other significantly changed species), because of the possible
349 horizontal inhomogeneity of HOM precursors and oxidants below the canopy. However,
350 our conclusion was confirmed by the incompatibility between the increasing ground
351 MT and CO₂ concentrations and the advection hypothesis (i.e., all species would show
352 similar tendencies if advection played a major role), indicating the influence of
353 horizontal and vertical advection is probably minor when compared to the increasing
354 sink. However, more direct evidence is still needed for further validation, which
355 highlights the need for joint vertical-planar HOM studies, measuring both vertical and
356 horizontal distribution of HOM concentrations.

357

358 **Conclusion**

359 Highly oxygenated molecules (HOMs) were measured above the canopy and at ground
360 level (below the canopy) in a boreal forest environment during the IBAIRN campaign
361 that took place in September 2016. Boundary layer dynamics and micrometeorology
362 were found to be important factors that influence the abundance and trends of HOMs
363 at ground level, by perturbing both their sources and sinks. In the well-mixed boundary
364 layer (e.g. during daytime or nights without strong inversion), HOM concentrations and
365 other measured species were overall similar between the ground and tower
366 measurements. In contrast, much lower ground level HOM concentrations were
367 observed when nighttime temperature inversion and formation of a decoupled layer
368 occurred below the canopy. On one hand, the production of the ground-level HOMs
369 could be affected by the decreasing O₃ concentrations and the increasing MT
370 concentration in the shallow layer. On the other hand, the surface area to volume ratio
371 dramatically increased in the shallow layer compared to the nocturnal boundary layer.
372 The possibility of losses on surfaces for ground-level HOMs became much larger than

373 usual during inversion nights. The enhanced interaction of air in the decoupled layer
374 with the forest floor was supported by increased concentrations of CO₂, emitted mainly
375 from the ground, in this layer.

376

377 We have presented the first detailed measurements of HOMs below and above the
378 canopy across a wide range of atmospheric stability conditions. The results highlight
379 the significance of near-ground boundary layer dynamics and micrometeorological
380 processes to the ambient HOMs, showing that ground-based HOM measurement might
381 not be representative for the entire nocturnal boundary layer. Conventionally, field
382 measurements of HOMs and other parameters are mostly performed close to **the** ground,
383 and the effect **of** boundary layer dynamics and micrometeorological processes to the
384 HOM **concentrations** have rarely been considered. Aerosol particle growth and SOA
385 formation rates at ground level are likely to be influenced by the reduced HOM
386 concentrations **in the inversion nights**. Clearly, more vertical and planar measurements
387 of HOMs are needed to confirm the emerging picture presented here. Influence **of**
388 boundary layer dynamics should be better characterized and evaluated in future field
389 campaigns.

390

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