

We thank the editor for the additional comments. The editor's comments are listed below and are followed by our replies (in italics).

Comments to the Author:

I have two major concerns on this manuscript and encourage the authors to elaborate more about the points below.

1. The major concern, as both reviewers address, is the instrumental or sampling biases due to the missing inter-comparison and horizontal separation in their set-up, during the mission. I do understand the limitations in real mission, so I suggest the authors to conduct more lab tests to address the relative TE (transmission efficiency) dependence of two instruments on various meteorological parameters; repeat figure 1 type experiments for different parameters such as temperature, pressure and RH to verify the possible biases in instruments in quantitative way. (The ionization efficiency may vary with that kinds of parameters.).

In order to address the editor's concern about the potential biases due to the missing inter-comparison and horizontal separation, we now performed a side-by-side inter-comparison at the site from June 15 to 21, 2018. The "tower" CI-APi-TOF was deployed to the container where ground measurement was conducted and measured together with the "ground" CI-APi-TOF for 6 days. Figure R1 shows ambient temperature, RH, and the total HOM concentrations measured by the "ground" and "tower" CI-APi-TOFs during the inter-comparison. Clear variations of ground temperature (from 6.6 °C to 24.5 °C) and RH (27 % to 100 %) were observed, but a good agreement ($R^2=0.91$, as shown in Figure R2) could still be found between the concentrations obtained from the two instruments, which confirmed that the two CI-APi-TOFs are comparable, and their consistency is not biased by ambient temperature or RH change. The "ground" total HOM concentrations in Figure R1 were not corrected by the relative TE (transmission efficiency) curve, thus in Figure R1 there is a nearly constant ratio (a factor of 6, as also shown in Figure R2) between the concentrations from "ground" and "tower" instruments. This difference is in good accordance with the TE curve shown in Figure 1 in our manuscript.

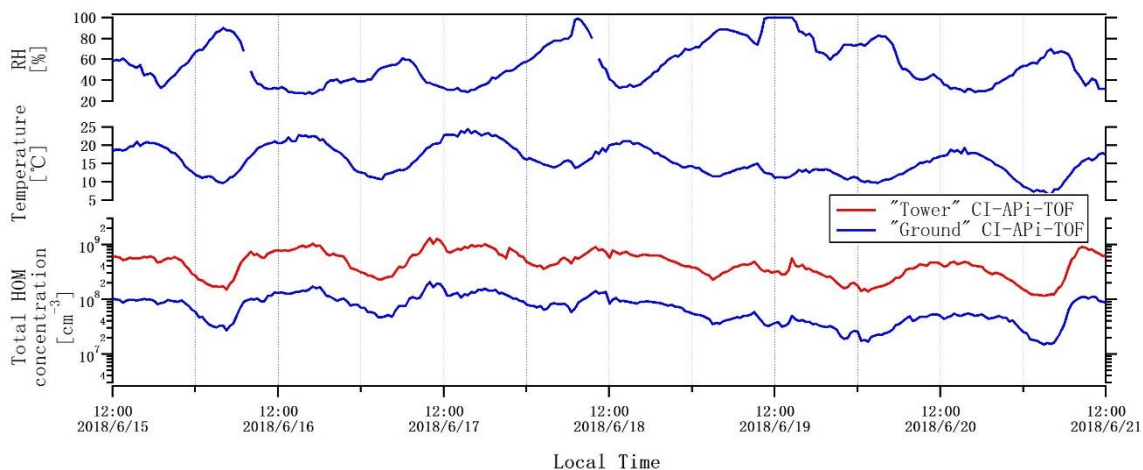


Figure R1 Time series of RH, temperature, and total HOM concentration measured by the "ground" and "tower" CI-APi-TOFs during the side-by-side inter-comparison from June 15 to 21, 2018.

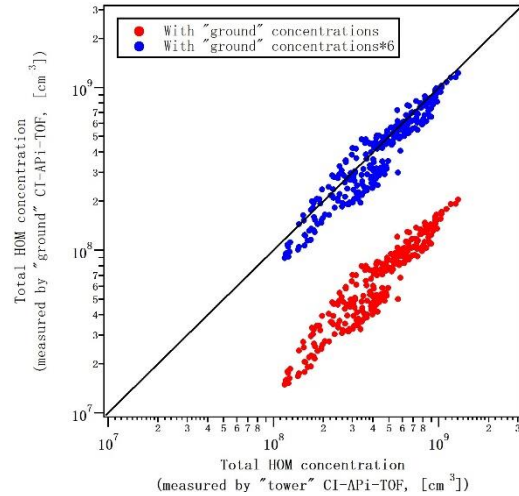


Figure R2 Correlation between total HOM concentrations measured by “ground” and “tower” CI-API-TOFs (red circles), and correlation after multiplying concentration from “ground” instrument by a factor of 6 (blue circles).

For comparison, Figure R3 shows ambient measurement data from May 24 to 30, 2018, shortly before the side-by-side inter-comparison. The most significant nighttime temperature inversion during this period was observed in the night of May 24, with a maximum ground and tower temperature difference of -6.5 °C. The tower total HOM concentrations were generally stable or increased slightly during the night. In contrast, the ground concentrations kept decreasing until temperature inversion disappeared, after which the instruments again track each other closely. Similar opposite patterns between the two instruments were also observed in other inversion nights during this week, all analogous to our measurements in 2016.

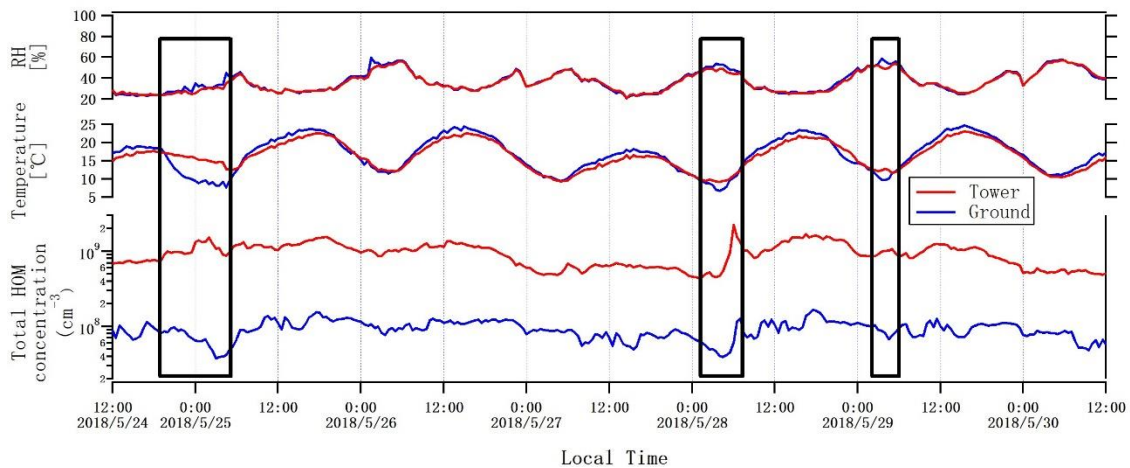


Figure R3 Time series of RH, temperature, and total HOM concentrations at ground and tower levels during field measurement from May 24 to 30, 2018. Nights with temperature inversion are framed with black rectangles.

Furthermore, there is no indication from both experimental and theoretical studies shows that the large differences observed during inversion nights in our study were due to the changes in the instrumental response to changing ambient parameters, such as RH, temperature, and pressure:

1. *RH: In the chemical ionization mass spectrometry community, it has long been known that reagent ions (such as nitrate) that form dimers with their neutral precursor (nor nitrate: $\text{HNO}_3 \cdot \text{NO}_3^-$) are much less impacted by humidity than reagent ions that do not form dimers (e.g. I, Br⁻). This was recently concluded specifically for HOM utilizing a completely theoretical approach (Hyytinen et al., 2018) For the case of iodide CIMS (CI-APi-TOF), Lee et al. (2014) tested the humidity dependence and the results show that the change in sensitivity under any reasonable ambient conditions is less than a factor 2. Considering that iodide is going to be much more sensitive to humidity changes than the nitrate-based CI-APi-TOF, we argue that the nearly order-of-magnitude changes in HOM concentrations that we observed in our study are highly unlikely to be caused by changes in instrument sensitivity due to changes in RH.*
2. *Temperature: Both instruments are housed in temperature-controlled containers, and as such, even though ambient temperature changes, the instrument temperature does not. The sampled air (7 LPM) is mixed with a larger sheath flow (35 LPM, at room temperature), which severely dampens any changes in sample flow temperatures already in the inlet. This is of course also the case for RH in point 1.*
3. *Pressure: The temporal pressure variation during our study period was on the order of one percent. The difference in pressure between ground and tower, on the other hand, based on the hydrostatic equation, is around 5mbar, i.e 0.5 %. This value itself will have varied only a negligible amount. These pressure changes are very small, and we are not aware of any physical process that could cause a measurable change in our instrumental response due to these variations. The charging of most HOM is governed by the collision rate of HOM molecules with the charging ions (Ehn et al., 2014), as the formed $\text{HOM} \cdot \text{NO}_3^-$ clusters are thermodynamically extremely stable (Hyytinen et al., 2015).*

We sincerely hope that our new measurements together with the above argumentation adequately address all of the editor's concerns on this subject.

2. If the measurements were conducted within the roughness sublayer, point measurement likely have limitations in inferring larger scale exchange (Raupach, M. R. 1987). More cautious descriptions are required for the implication part of this manuscript unless the authors describe more about the turbulent characteristic at the site.

We make below modifications to the manuscript to have a more cautious description of the implication.

In the abstract part, we add:

“However, much lower HOM concentrations were frequently observed at ground level, which was likely due to the formation of a shallow decoupled layer below the canopy.”

AND

“Our findings also illustrate that near-ground HOM measurements conducted in strong stably stratified conditions at this site might only be representative of a small fraction of the entire nocturnal boundary layer.”

In the introduction part, we modify below text from:

“...the HOMs at these different heights are explicitly analyzed and characterized in conjunction with auxiliary turbulence and micrometeorological measurements.”

To

“...the HOMs at these different heights at SMEAR II station are analyzed and characterized in conjunction with auxiliary turbulence and micrometeorological measurements.”

In the conclusion/implication part, we add:

“..., showing that ground-based HOM measurement at this site might not be representative for the entire nocturnal boundary layer.”

AND

“, and the possible effect of boundary layer dynamics and micrometeorological processes to the HOM concentrations have rarely been considered”

A sentence is added to point out that the implication is still limited by the current experiment design:

“However, there are still limitations due to current experiment design, such as horizontal separation in instrument set-up, or the uncertainties from using point measurements at two heights to infer larger scale exchange.”

We also add below text to Section 3.1 to describe more details about turbulent characteristics at the measurement site:

“...a total leaf area index (LAI) of $\sim 6.5 \text{ m}^2 \text{ m}^{-2}$, a stand density of $\sim 1400 \text{ trees ha}^{-1}$, and an average diameter at breast height (DBH) of $\sim 0.16 \text{ m}$ (Bäck et al., 2012; Launiainen et al., 2013). The forest floor is majorly covered with a shallow dwarf shrub (a LAI of $\sim 0.5 \text{ m}^2 \text{ m}^{-2}$) and moss layer (a LAI of $\sim 1 \text{ m}^2 \text{ m}^{-2}$) (Kulmala et al., 2008; Launiainen et al., 2013).”

Minor comments

Error or uncertainty analysis on the gradient of HOM would be helpful to convince the reader; more scatter on higher m/z in figure 1 may also derive the large variation in higher m/z in figure 8 and 9. Quantitative description about HOM difference would be plausible to proof the existence of HOM.

We are not sure if we interpret the editor's comments correctly but have now added discussion on the uncertainties in the HOM concentration estimates. However, concerning the last sentence, we do not feel that the existence of HOM is beyond any doubt at this stage, considering the wealth of studies on the topic.

In order to determine uncertainties in concentration estimations between the two instruments, and to account for error related to the assumption of strong mixing leading to equal concentrations at the tower and ground during daytime, we compared the sulfuric acid signals between the two instruments. Figure S1 (now added to the SI) shows scatter plots between ground and tower sulfuric acid (SA) signals from 08:00 to 16:00 LT. During nighttime (before 07:00 and after 17:00), sulfuric acid concentrations were very low, sometimes below detection limit, and therefore were not included in this figure. At 08:00 and 16:00 LT, vertical turbulent mixing was still weak, and ground and tower experiments might be experiencing different turbulent mixing strength, thus lower coefficients of determination were obtained ($R^2=0.35$ at 08:00 LT, and 0.86 at 16:00 LT). However, from 09:00 to 15:00 LT, a uniform (well-mixed) boundary layer condition occurred. Strong correlations (all R^2 were higher than 0.97) were found between the two heights, and an average instrumental error of $\sim 26\%$ could be obtained based on all the measured tower/ground sulfuric acid ratios during this period.

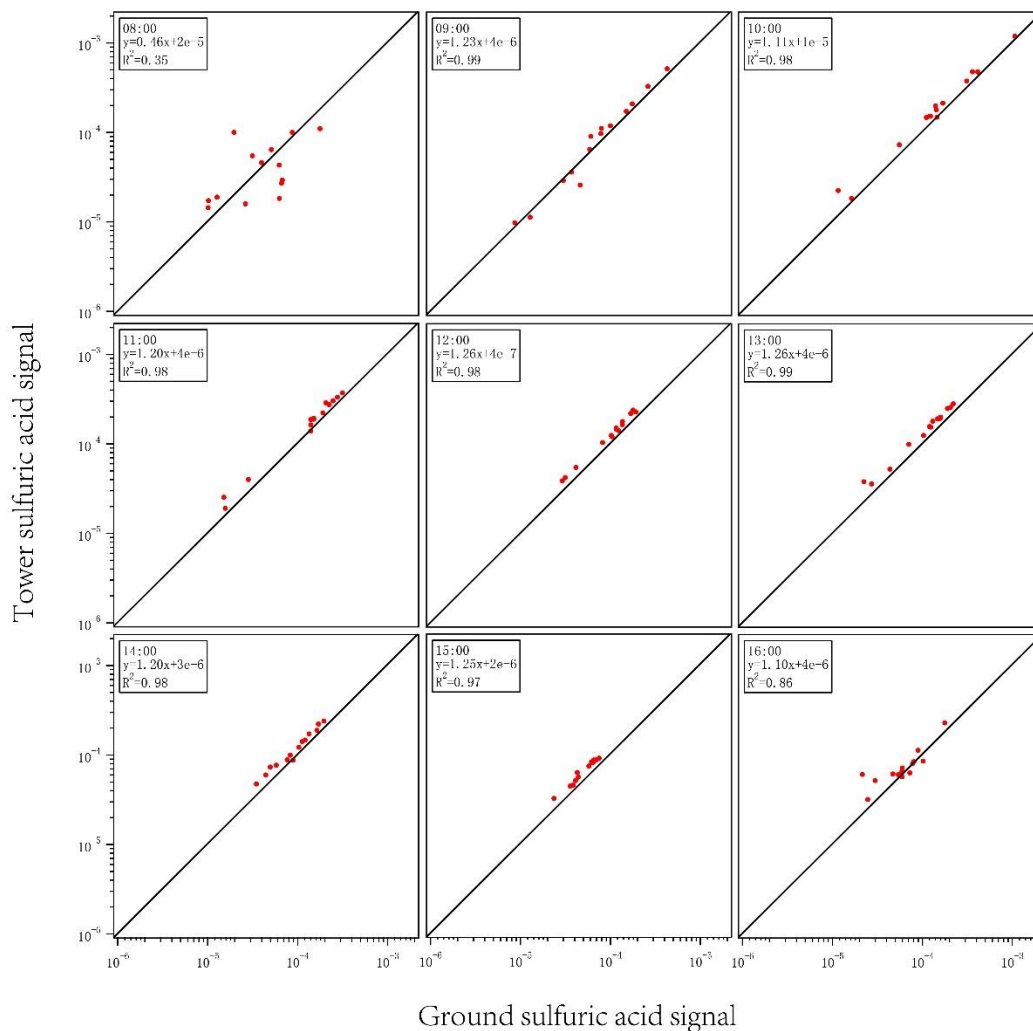


Figure S1 Correlation between ground and tower sulfuric acid signals from 08:00 – 16:00 LT (1-hour averaged, normalized to reagent ions) during campaign. The black line denotes 1:1 ratio.

Next, we calculated the error associated with the TE correction. An average error of ~10% was determined from the higher mass range (m/z 500 - 600) in Figure 1, which could be considered as the upper limit of the error from our regression. From these two errors (instrumental and regression), we can calculate an estimate of the total error using the method of error propagation. The resulting value is ~28%, which can be compared to the two case studies in Figure 5. The average total HOM concentrations during the non-inversion night differed by $(\text{total HOM in tower}) / (\text{total HOM at ground}) = \sim 20\%$ while during the inversion night they differed by ~265%. While 20% is within/close to the calculated uncertainty of 28%, the difference during the inversion night (265%) is clearly larger and significant.

Below text is added to Section 3.2 to describe the uncertainty from HOM vertical gradient in a more quantitative way:

“To test our assumption of negligible vertical gradients of HOMs during daytime, we analyzed the behavior of sulfuric acid. We found that the uncertainty related to this assumption

corresponds to a value of 26% (see Figure S1). An upper limit of uncertainty relating to our TE correction (Figure 1) was also estimated, yielding a value of 10%, giving a total uncertainty from these two sources of 28%. This value is much smaller than the observed deviation of HOM concentrations during inversion nights (e.g. Figure 5)."

2. Address the physical meaning of curve fitting in figure 1.

The physical meaning of the curve fitting is to make the two instruments directly comparable, by removing differences in the mass-dependent transmission of ions through the two CI-APi-TOF instruments. The transmission of a certain instrument depends on multiple factors, including the detailed alignment of all part inside the instrument, exact pressures at each of the different stages, voltage settings, etc. For a thorough description of different parameters influencing the ion transmission, we refer to section 2 "Mass discrimination effects" in Heinritzi et al. (2016).

As stated by Heinritzi et al. (2016), it is basically impossible to calculate the transmission efficiency, and in practice it needs to be experimentally determined. For determining exact concentrations, this needs to be done through fairly tedious calibrations. In our case, where we only compare two instruments relative to each other, it was sufficient to scale the instruments to each other during periods when they were measuring the same sample (i.e. the turbulent, noon-time period).

To better clarify the physical meaning of the fitted curve, we add below texts to Section 3.2:

"For a detailed discussion on factors affecting the TE of a CI-APi-TOF, we refer to Heinritzi et al. (2016)."

AND

"A fitted relative TE curve ($R^2 = 0.97$), which represents how the TE of the tower CI-APi-TOF was changed at each m/z over the TE of the ground one, was obtained using power law regression."

3. Any temperature, RH, pressure dependence in 1:1 correlation between tower and ground HOM? (I mean figure 3 colored by different variables.)

As shown in Figure R4, points with different colors can be seen on the 1:1 line in each subplot, indicating that the vertical distribution of noontime HOM concentrations were not strongly depending on temperature, RH, or air pressure. Monoterpene emissions (which are HOM precursors) have a strong temperature dependence, and therefore the higher temperature show higher HOM concentrations (at both heights).

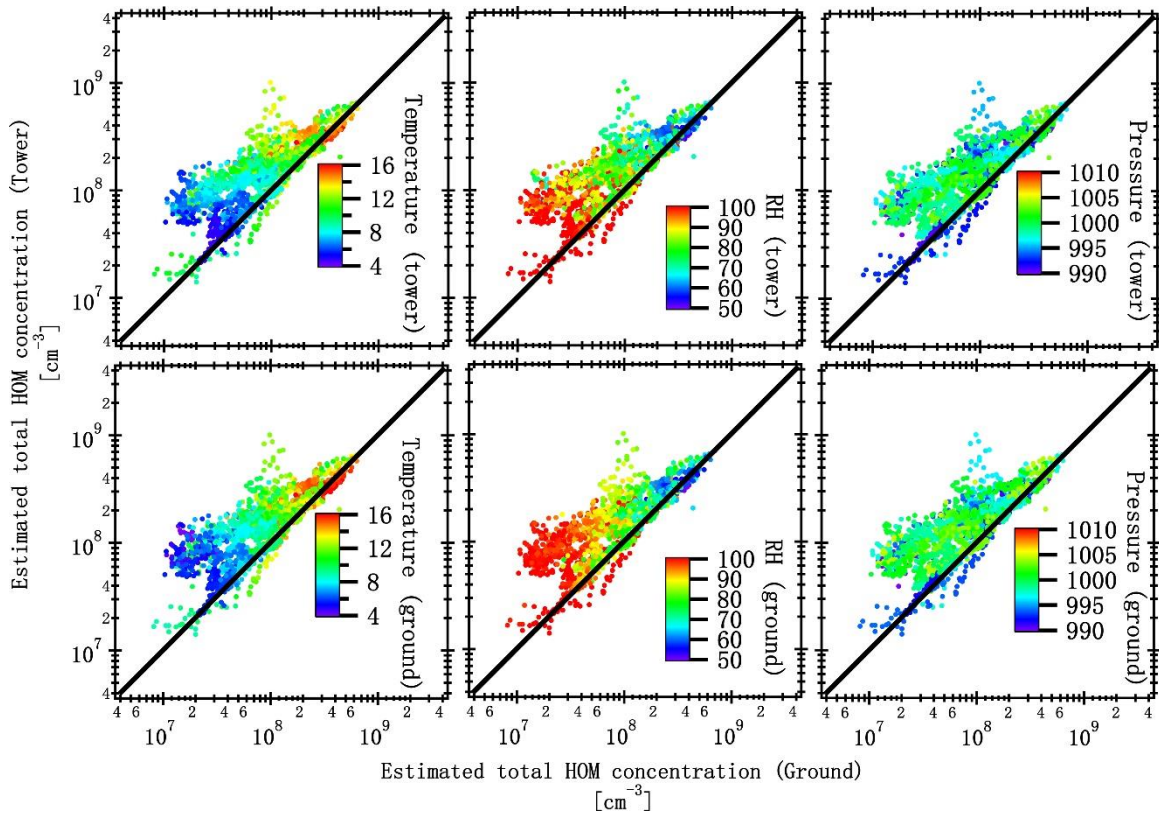


Figure R4 Correlations between ground and tower HOM measurements. The black lines denote 1:1 ratio. Color codes indicate temperature (left), RH (middle) and pressure (right) measured at ground (lower row) and tower (upper row) levels.

4. If the authors put the information in Table 1 as box whisker plots, that would be easy to read

We agree that there were too many numbers in Table 1. As the main point of the table was to show the significant difference between non-inversion and inversion nights, we realize that the mean and median values are already capable in doing that. Thus, we delete the rows of 25/75 percentile data in Table 1, to simplify the table and make it easier to read.

5. Brief mention and more discussion about condensation sink would be helpful to the readers who are not in this field.

Below texts are added to the Section 4.3.2:

“A rapid decrease was found in CS, which represents the rate of condensation of low-volatile vapors onto the existing aerosol particles (Dada et al., 2017), implying that the aerosol population was also altered.”

AND

“However, all the HOM groups showed significant decrease after midnight, despite the CS (generally the main sink for HOM in the atmosphere) staying practically constant.”

6. Difference or ratio plot between tower and ground for figure 7 would be more informative; current plot has many overlaps in points. This part may have a chance to link with figure 8 and 9 for deeper analysis than descriptive results.

Modified, Figure 7 is changed to:

“

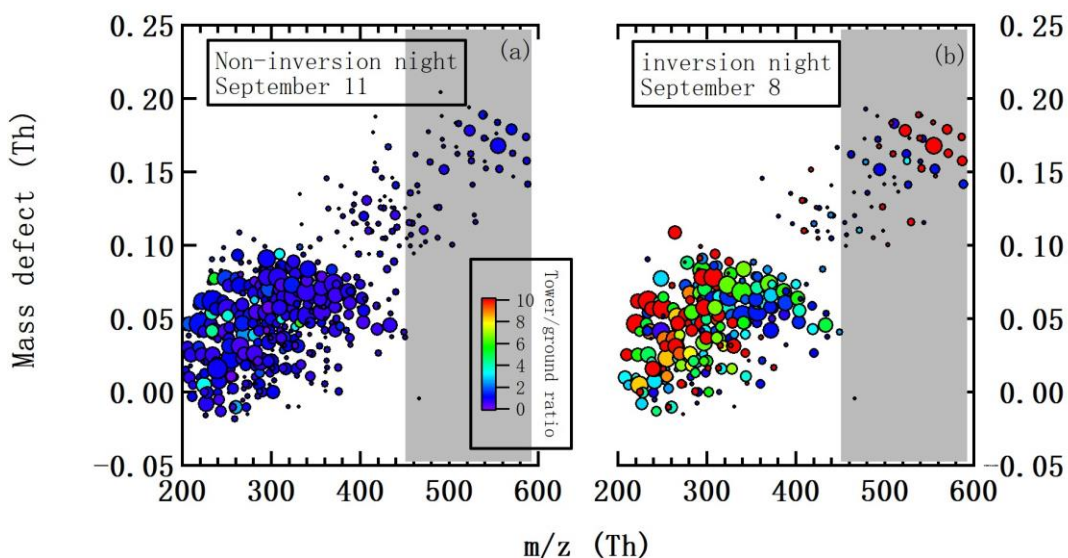


Figure 7 Mass defect (MD) plots of the selected (a) “non-inversion night” case (September 11); and (b) “inversion night” case (September 8). Color code indicates the ratios between tower/ground HOM concentrations. Grey shade area denotes the dimer range (m/z 450-600).

”

And we also modify below texts from:

“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.”

To

“The mass defect (MD) plot (Figure 7) separates all identified compounds according to their exact masses on the x-axis and the deviation from the integer mass on the y-axis. Each circle represents a compound, with the areas scaled by concentrations, and colored by the ratios between tower and ground concentrations. Figure 7a and 7b are MD plots showing the mean spectra of the selected non-inversion night (September 11) and inversion night (September 8).

Without the formation of a decoupled layer, nearly the same concentration distributions of HOMs were observed. In contrast, during the inversion night (September 8, Figure 7b), large differences could be found between the two measurement heights.”

7. If possible, I suggest the authors to add figure R1 for all time windows of a day in supplement as a way to prove the gradient in HOM is real.

Added, see Figure S1 in previous response.

8. I feel the description about the forest are missed in this manuscript especially for the readers who are not familiar with the site. Description about the canopy structure parameters (i.e. LAI, leaf distribution, tree species etc.) are required not only for the turbulent characteristics but also for the sources and sinks of HOM. I also suggest the authors to add a schematic of the site including the information about all the measurements which took place at the site to ease the reader for that information.

A description of forest structure and other parameters were added, see previous response. Below schematic figure of the site was added to the supplementary file as Figure S2.

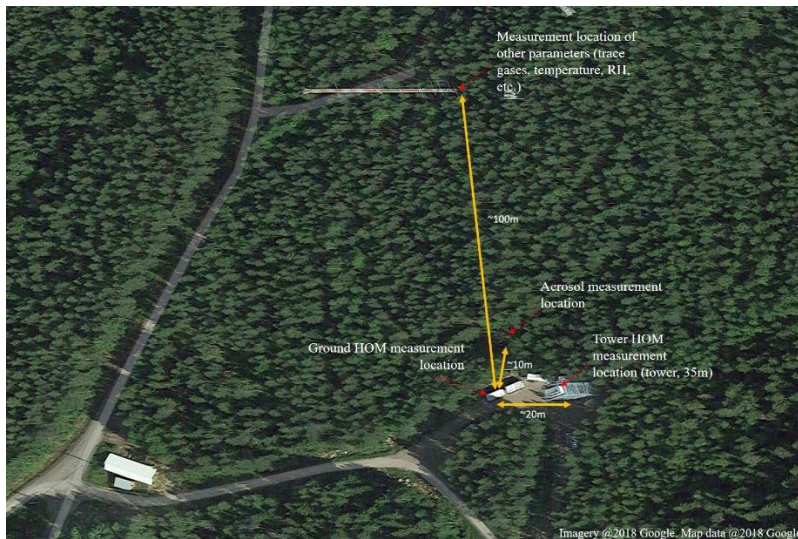


Figure S2 Map from Google Earth showing locations of all the measurements during IBAIRN campaign at SMEAR II station.

We also add below text in Section 3.2:

“A schematic figure showing locations of all the measured parameters used in this study is provided in Figure S2.”

Reference:

- Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q. and Boy, M.: Chemodiversity of a Scots pine stand and implications for terpene air concentrations, *Biogeosciences*, 9(2), 689–702, doi:10.5194/bg-9-689-2012, 2012.
- Dada, L., Paasonen, P., Nieminen, T., Mazon, S. B., Kontkanen, J., Peräkylä, O., Lehtipalo, K., Hussein, T., Petäjä, T., Kerminen, V.-M., Bäck, J. and Kulmala, M.: Long-term analysis of clear-sky new particle formation events and nonevents in Hyytiälä, *Atmos. Chem. Phys.*, 17, 6227–6241, doi:10.5194/acp-17-6227-2017, 2017.
- 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.
- 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.
- Hyttinen, N., Kupiainen-Määttä, O., Rissanen, M. P., Muuronen, M., Ehn, M. and Kurtén, T.: Modeling the Charging of Highly Oxidized Cyclohexene Ozonolysis Products Using Nitrate-Based Chemical Ionization, *J. Phys. Chem. A*, 119(24), 6339–6345, doi:10.1021/acs.jpca.5b01818, 2015.
- Hyttinen, N., Otkjær, R. V., Iyer, S., Kjaergaard, H. G., Rissanen, M. P., Wennberg, P. O. and Kurtén, T.: Computational Comparison of Different Reagent Ions in the Chemical Ionization of Oxidized Multifunctional Compounds, *J. Phys. Chem. A*, 122(1), 269–279, doi:10.1021/acs.jpca.7b10015, 2018.
- Kulmala, L., Launiainen, S., Pumpanen, J., Lankreijer, H., Lindroth, A., Hari, P. and Vesala, T.: H₂O and CO₂ fluxes at the floor of a boreal pine forest, *Tellus, Ser. B Chem. Phys. Meteorol.*, 60 B(2), 167–178, doi:10.1111/j.1600-0889.2007.00327.x, 2008.
- Launiainen, S., Katul, G. G., Grönholm, T. and Vesala, T.: Partitioning ozone fluxes between canopy and forest floor by measurements and a multi-layer model, *Agric. For. Meteorol.*, 173, 85–99, doi:10.1016/j.agrformet.2012.12.009, 2013.
- Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T. K., Worsnop, D. R. and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, , doi:10.1021/es500362a, 2014.

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

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1 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, **which was likely** due to the

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

40 **2 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 ($CHON_{\text{monomer}}$). 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 $CHON_{\text{monomer}}$, 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 ($CHON_{\text{dimer}}$), 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 **at SMEAR II station**
110 are analyzed and characterized in conjunction with auxiliary turbulence and
111 micrometeorological measurements.

112 3 Experimental

113 3.1 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, a total leaf area index (LAI) of ~6.5 m²m⁻²,
121 a stand density of ~1400 trees ha⁻¹, and an average diameter at breast height (DBH)
122 of ~0.16 m (Bäck et al., 2012; Launiainen et al., 2013). The forest floor is majorly
123 covered with a shallow dwarf shrub (a LAI of ~0.5 m²m⁻²) and moss layer (a LAI of ~1
124 m²m⁻²) (Kulmala et al., 2008; Launiainen et al., 2013). The planetary boundary layer
125 height at the SMEAR II station has been determined from previous studies using
126 radiosondes (Lauros et al., 2007; Ouwersloot et al., 2012) and balloon soundings
127 (Eerdekens et al., 2009). Roughly, these heights span some 400 m (March) to 1700 m
128 (August) at noontime, and 100 m (March) to <160 m (April) at midnight.

129 3.2 Instrumentation

130 Concentration of HOM molecules were measured with two nitrate-ion based CI-APi-
131 TOF mass spectrometers. The CI-APi-TOF measuring at higher altitude was deployed
132 at the top of a 35 m tower located ~20 m horizontally from the ground measurement
133 location. Both instruments were working in rooms with air-conditioning and room
134 temperatures controlled at 25 °C. The inlets of the two instruments were pointed to the
135 southeast direction and fixed at ~36 m and ~1.5 m above ground. The tower
136 measurement is about twice the canopy height, which is still within the roughness
137 sublayer of the forest (Raupach and Thom, 1981). The instrument setup of the two CI-

138 APi-TOF mass spectrometers were similar. In brief, the CI-APi-TOF was the
139 combination of a chemical ionization (CI) inlet, and an atmospheric pressure interface
140 time-of-flight (APi-TOF) mass spectrometer (Aerodyne Research Inc., USA, and
141 ToFwerk AG, Switzerland). The ambient air was first drawn into the inlet with a sample
142 flow of 7 lpm (liter per minute), and then centered to an ion reaction tube surrounded
143 by sheath flow (filtered air, 35 lpm). Meanwhile, the nitrate ions carried by the sheath
144 gas, which were generated by exposing the nitric acid (HNO_3) to soft x-ray radiation,
145 were guided into the sample gas by an electrical field at ambient pressure (~ 100 ms
146 reaction time). Neutral molecules (M) in the sample air were ionized by either
147 clustering with charged nitrate/nitric acid ($(\text{HNO}_3)_{n=0-2} \cdot \text{NO}_3^-$) to form $(M) \cdot \text{NO}_3^-$ cluster
148 ions, or losing a proton to the charging ions to form deprotonated ions (e.g.,
149 $\text{H}_2\text{SO}_4 + \text{NO}_3^- \rightarrow \text{HSO}_4^- + \text{HNO}_3$). The ions then entered the APi part, which was a three-
150 stage vacuum chamber, through a pinhole. In the APi, two quadrupoles and stack of ion
151 lenses guide the ions into the TOF mass spectrometer, where ions were separated based
152 on their mass-to-charge (m/z) ratios. A more detailed description of this instrument has
153 been given by Junninen et al. (2010) and Jokinen et al. (2012). Mass spectra obtained
154 from the instrument were analyzed using the ‘tofTools’ program described in Junninen
155 et al. (2010). Determination of the concentration of a measured molecule M was based
156 on the following equation:

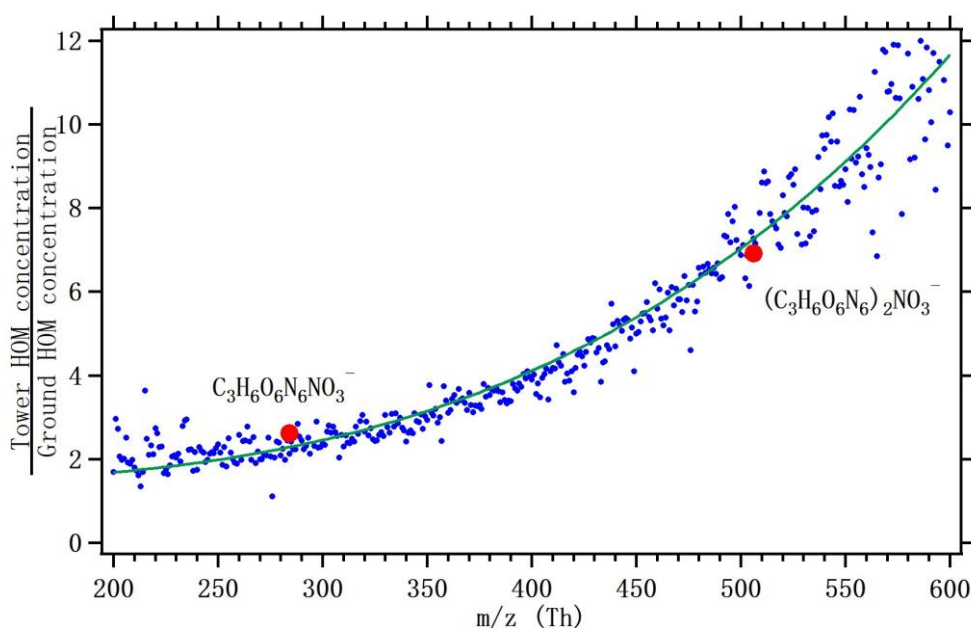
$$157 \quad [M] = \frac{\sum M}{\sum \text{reagent ion count rates}} \times C \quad (1)$$

158 where the sum of ion count rates was an inclusion of all detected ions relating to
159 compound M , whether deprotonated or in clusters with reagent ions, and the sum of
160 reagent ion count rates is the total signal of the charged nitric acid ions. C was the
161 calibration coefficient, which was assigned the same value for all detected compounds.
162 This assignment is only valid for compounds that cluster with the reagent ions at the
163 collision limit, such as H_2SO_4 (Viggiano et al., 1997) and have equal collision rates.
164 The collision rates of nitrate ions with H_2SO_4 and with HOMs are expected to be very
165 close (Ehn et al., 2014). Here, a calibration coefficient of 1×10^{10} molec cm^{-3} , estimated

166 from previous calibrations with similar settings using sulfuric acid and theoretical
167 constraints (Ehn et al., 2014), with an uncertainty of at least -50%/+100%, was used in
168 calculating the HOM concentrations for both instruments. Ultimately, the absolute
169 HOM concentrations in this work are of secondary importance, as we focus on the
170 relative comparison of HOM concentrations measured at different heights. However,
171 the comparability of the two CI-APi-TOF instruments is of great importance, and
172 results cannot be allowed to vary e.g. as a result of inevitable differences in the mass-
173 dependent transmission efficiency (TE). For a detailed discussion on factors affecting
174 the TE of a CI-APi-TOF, we refer to Heinritzi et al. (2016). To this end, instead of
175 directly evaluating the TE of each instrument, a “relative” TE of the two CI-APi-TOFs
176 was used for data correction: we selected a time period at noon-time on September 9
177 with well-mixed boundary layer condition, identified with the clear and sunny weather
178 and homogeneous vertical distribution of monoterpene and other trace gases., and
179 assumed the HOM concentrations at the two heights to be the same. Thus, the relative
180 TE was obtained from the concentration ratio between the two CI-APi-TOFs at each
181 m/z (Figure 1). A fitted relative TE curve ($R^2 = 0.97$), which represents how the TE of
182 the tower CI-APi-TOF was changed at each m/z over the TE of the ground one, was
183 obtained using power law regression. Weaker correlation was obtained in the 200-250
184 and 500-600 Th mass ranges, but in the mass range where most of the HOMs were
185 located (290-500 Th) there is very little scatter around the fitted curve, clearly
186 suggesting that observed differences in the two instruments responses were mainly due
187 to differences in TE. To test our assumption of negligible vertical gradients of HOMs
188 during daytime, we analyzed the behavior of sulfuric acid. We found that the
189 uncertainty related to this assumption corresponds to a value of 26% (see Figure S1).
190 An upper limit of uncertainty relating to our TE correction (Figure 1) was also estimated,
191 yielding a value of 10%, giving a total uncertainty from these two sources of 28%. This
192 value is much smaller than the observed deviation of HOM concentrations during
193 inversion nights (e.g. Figure 5). Additionally, an inter-comparison between the two

194 instruments with a permeation tube containing trinitrotriazinane ($C_3H_6N_6O_6$) was
195 conducted in the field right after the campaign. The results showed good agreements
196 with the relative TE, lending confidence to the method used here. Finally, it should be
197 noted that the difference in TE between the two instruments was larger than one would
198 normally expect, since the tower CI-APi-TOF had been tuned for higher sensitivity at
199 the largest masses (at the expense of transmission at the lower masses).

200



201

202 Figure 1 The relative TE curve between the two CI-APi-TOF mass spectrometers. Inter-comparison
203 results using a permeation tube containing trinitrotriazinane ($C_3H_6N_6O_6$) are shown in red circles.

204

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

209

210 The MT, trace gases, and meteorological parameters were continuously monitored at
211 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)
212 on a 126 m mast ~100 m away from the location of the CI-APi-TOFs. The data at 4.2

213 m and 33.6 m were used in this study to represent the concentrations at near ground and
214 tower level, respectively. Ambient MT concentration was measured every third hour
215 using a proton transfer reaction mass spectrometer with a lower detection limit of 1
216 pptv (PTR-MS, Ionicon Analytik GmbH; Taipale et al., 2008). The O₃ concentration
217 was measured with an UV light absorption analyzer that had a lower detection limit of
218 1 ppbv (TEI model 49C, Thermo Fisher Scientific, USA). The NO_x measurement was
219 conducted using a chemiluminescence analyzer (TEI model 42C TL, Thermo Fisher
220 Scientific, USA). The lower detection limit of the NO_x analyzer is 100 pptv. The CO₂
221 measurement was performed using an infrared detection system (LI-840, LiCor
222 Biosciences, Lincoln, NE, USA). The aerosol number concentration size distributions
223 were obtained with a twin differential mobility particle sizer (twin-DMPS) for the size
224 range from 3-1000 nm (Aalto et al., 2001) at 8 m height above ground, and was used to
225 calculate condensation sink (CS) based on the method from Kulmala et al. (2001). Air
226 temperature was measured with PT-100 resistance thermometers. Air relative humidity
227 (RH) was measured with RH sensors (Rotronic Hygromet model MP102H with
228 Hygroclip HC2-S3, Rotronic AG, Switzerland). Global radiation (solar radiation in
229 wavelength range of 0.3-4.8 μm) was obtained with a Pyranometer (Reemann TP3,
230 Astrodata, Estonia) above the canopy top at 18 m. All the data presented are at 10 min
231 averaging intervals, except for the MT (in 1-hour averaging interval). **A schematic**
232 **figure showing locations of all the measured parameters is provided in Figure S2.**

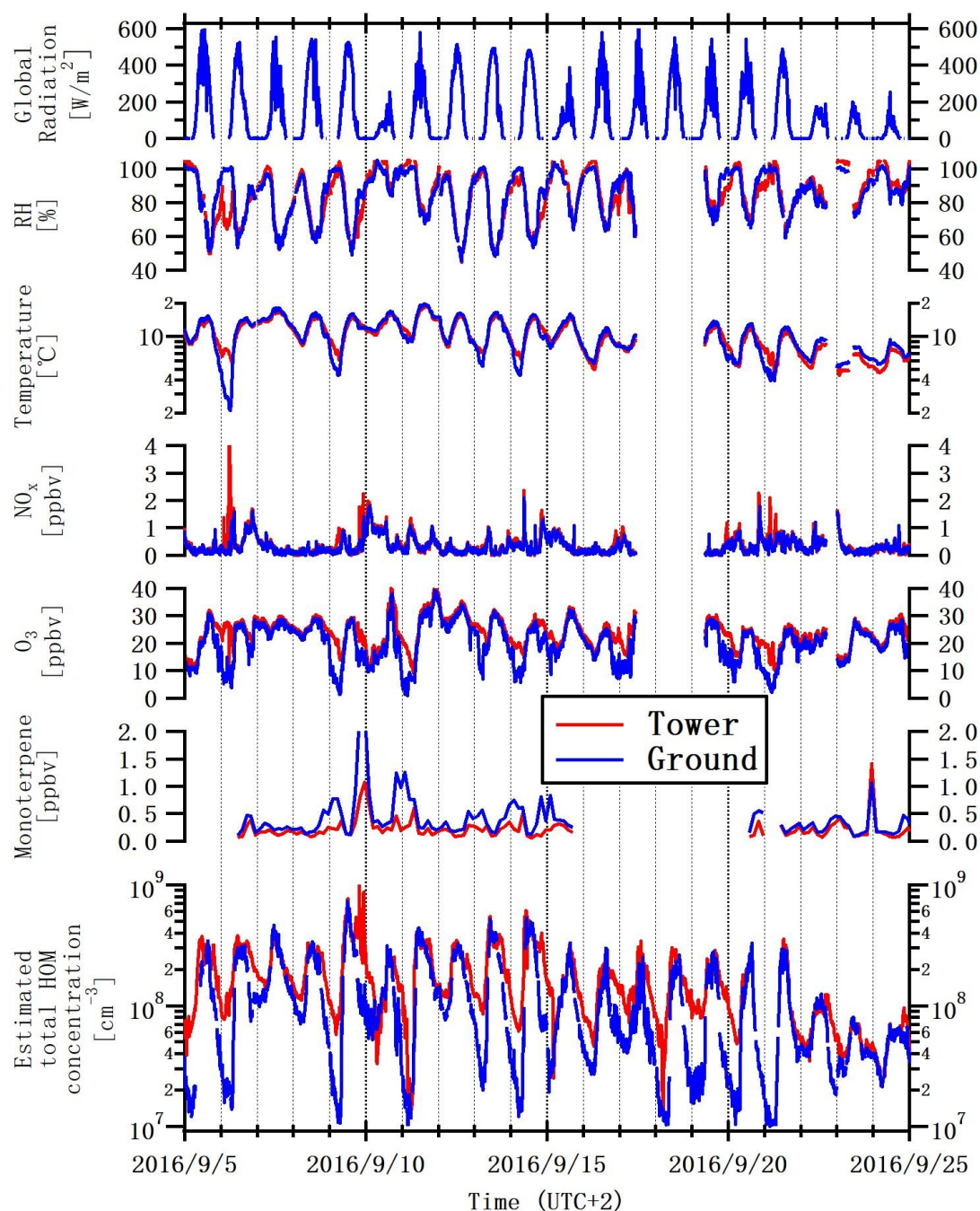
233

234 **4 Results and discussion**

235 **4.1 Data overview**

236 The Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget
237 (IBAIRN) campaign was conducted from September 1 to 25, 2016. After data quality
238 checks, only the measurements collected after September 5 were used. Figure 2 shows
239 the overall time series of the meteorological parameters measured at ground and tower

240 levels, including the temperature, RH, global radiation, concentrations of trace gases,
241 MT, and total HOMs. The weather was generally sunny and clear during the campaign
242 except for a few cloudy (September 10, 15, and 22-23) and drizzling (September 24
243 and 25) days. The mean air temperature and RH observed at ground level were $10.8 \pm$
244 3.3 °C and 87 ± 13 % (1σ standard deviation), and at the tower level were 10.5 ± 3.0 °C
245 and 88 ± 14 %, respectively. The O₃ concentrations measured at ground and tower levels
246 were 21 ± 8 ppbv and 25 ± 6 ppbv, respectively. The air temperature, RH and O₃
247 measured at the two heights were close to each other during daytime. The NO_x
248 concentrations were quite low throughout the campaign, the mean NO_x concentrations
249 were mostly around the reported detection limit at 0.4 ± 0.4 ppbv (ground) and $0.4 \pm$
250 0.5 ppbv (tower), yet showed an overall good agreement between the measurements at
251 the different heights. The MT concentrations at ground level (0.38 ± 0.34 ppbv on
252 average) were generally higher than that above the canopy level (0.20 ± 0.16 ppbv).
253



254

255 Figure 2 The overall time series of the measured trace gases, meteorological parameters and estimated
 256 total HOM concentrations at the ground (blue) and tower (red) levels.

257

258 The estimated total HOM concentration is representative for the overall concentration
 259 level of HOMs, and is defined as the sum of the detected signals between ions from m/z
 260 200 to 600 after removing the identified background peaks. The gaps in the ground
 261 estimated total HOM data were due to automatic zero-check. During the campaign, a

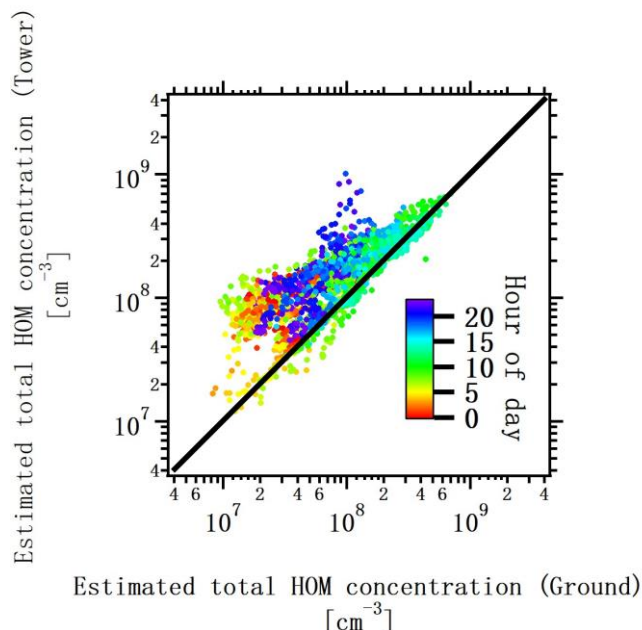
262 significant difference was found in the estimated total HOM concentrations below and
263 above the canopy (mean and median concentrations of $1.1 \pm 1.7 \times 10^8 \text{ cm}^{-3}$ and $7.6 \times$
264 10^7 cm^{-3} at ground level, $1.7 \pm 1.3 \times 10^8 \text{ cm}^{-3}$ and $1.3 \times 10^8 \text{ cm}^{-3}$ at tower level). The
265 causes of these differences ($\sim 55\%$ in mean and $\sim 71\%$ in median) frame the upcoming
266 discussion.

267

268 **4.2 Inter-comparison of estimated total HOM concentrations**

269 The estimated total HOM concentrations at the two heights were not different during
270 the day (mean $\pm 1\sigma$ standard deviation and median concentrations of $4.1 \pm 2.3 \times 10^8 \text{ cm}^{-3}$
271 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
272 level), which validates the use of only one day of data for scaling the TE of the ground
273 CI-APi-TOF to match the HOM signals. The good daytime agreement throughout the
274 campaign period also verifies that the response of each instrument stayed stable.
275 Contrary to the daytime results, the estimated total HOM concentration at ground level
276 usually diverged from the tower measurement in the nocturnal boundary layer. The
277 concentration below the canopy became even lower when temperature inversions were
278 observed, accompanied by a decreasing ground-level O_3 and increasing MT
279 concentrations. Figure 3 shows the correlation between the estimated total HOM
280 concentrations observed at two heights. Herein, good agreement could be found for the
281 group of points representing the concentrations around noontime ($R^2 = 0.89$). The
282 points indicating the nighttime estimated total HOM concentrations were scattered (R^2
283 $= 0.28$), and the ground concentrations were found to be much lower than the tower
284 ones.

285



286

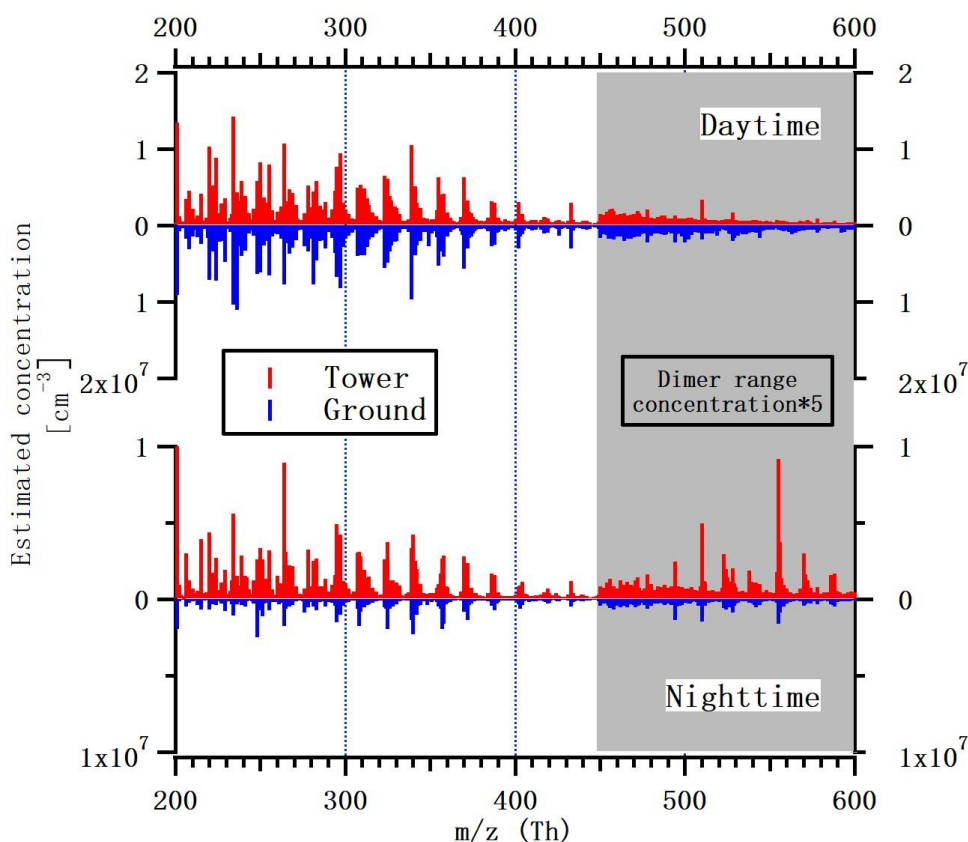
287 Figure 3 Correlation between ground (x-axis) and tower (y-axis) measurements of the estimated total
 288 HOM concentrations. The black line denotes 1:1 ratio. Color code indicates the sampling time of
 289 HOMs.

290

291 Figure 4 shows the mean mass spectra (in unit mass resolution, UMR, for m/z 200 –
 292 600) obtained from the ground and tower. It is worth mentioning that there might be
 293 some signals not attributable to HOMs in the plotted spectra, but only in little proportion.
 294 Only selected periods (09:00-15:00 for daytime and 21:00-03:00 for nighttime, local
 295 winter time (UTC +2)) are included in the averaging period to eliminate the effect of
 296 sunrise and sunset periods. During daytime, a good agreement ($R^2 = 0.87$) was obtained
 297 from the mass-by-mass comparison using the UMR concentrations extracted from
 298 daytime mean spectra, suggesting a uniform composition distribution in the daytime
 299 boundary layer condition. During nighttime, the mean concentrations of all HOM
 300 molecules in the ground mean spectra were much lower than the tower spectra. The
 301 HOM concentrations shown in the ground and tower mean spectra were also less
 302 correlated. Therefore, a logical outcome is that the conditions below and above the
 303 canopy are experiencing different turbulent mixing strength and/or source-sink regimes

304 during night.

305



306

307 Figure 4 Mean mass spectra with the averaging periods of daytime (09:00-15:00) and nighttime (21:00-

308 03:00) at ground and tower levels.

309 4.3 Influence of nocturnal boundary layer dynamics and micrometeorological 310 processes

311 The nighttime HOMs at ground level are likely influenced by transport processes below
312 the canopy, since the estimated total HOM concentrations were found much lower in
313 the nights when temperature inversions were observed. To further investigate the
314 potential impact of such micrometeorological phenomena on ground HOMs, for the
315 nights during the campaign without precipitation or instrument failure, were selected
316 (12 nights in total) and categorized into 2 types based on the occurrence of temperature
317 inversions: 1) the “non-inversion night” type included 6 nights when no temperature
318 inversion was recorded; 2) the “inversion night” type category consisted of 6 nights that

319 had encountered temperature inversions, and the ground temperatures were generally
320 ~ 1 °C lower than tower temperatures during these nights.

321

322 **4.3.1 Statistics of the “non-inversion night” and “inversion night” types**

323 Table 1 shows the overall statistics including the mean and median values of the
324 temperatures, O₃, NO_x, MT and estimated total HOM concentrations for the “non-
325 inversion night” and “inversion night” types. In the non-inversion nights, the air below
326 and above the canopy was relatively well-mixed. The mean and median concentrations
327 of the ground O₃ (21 ± 8 ppbv and 22 ppbv) were close to the tower values (25 ± 6 ppbv
328 and 24 ppbv). The slight difference might be attributed to the higher VOC emissions
329 (Rantala et al., 2014) and larger sink near ground level. In contrast, during the inversion
330 nights, the mean estimated total HOM concentration and O₃ at ground level were
331 generally much lower, only $\sim 33\%$ and $\sim 69\%$ of the tower concentrations, respectively.
332 Instead, the mean and median ground MT concentration (0.70 ± 0.28 ppbv and 0.70
333 ppbv) were ~ 3 times higher than the tower ones (0.24 ± 0.04 ppbv and 0.23 ppbv),
334 respectively. The measured NO_x levels were similar in both categories and heights,
335 though the ambient concentrations were close to the detection limit and therefore small
336 differences might not be observable.

337

338 **4.3.2 Case study**

339 Two individual nights representing the “non-inversion night” and “inversion night”
340 types were selected and further compared. Figure 5a shows the time series of the
341 meteorological parameters, trace gases and HOMs measured at ground and tower
342 levels of one selected night of “non-inversion night” type (September 11-12, from 21:00
343 to 03:00). A number of measures can be used to assess the local atmospheric stability
344 conditions at a given layer. These measures are commonly based on either the Obukhov

345 length and its associated atmospheric stability parameter or a Richardson number (flux-
346 based, gradient-based, or bulk). Because of its simplicity and the availability of high
347 resolution mean air temperature profiles, the bulk Richardson number (Ri) was used
348 here (Mahrt et al., 2001; Mammarella et al., 2007; Vickers et al., 2012; Alekseychik et
349 al., 2013). It is calculated using:

$$350 \quad Ri = \frac{g\Delta\bar{\theta}\Delta z}{\bar{\theta}(\bar{u})^2} \quad (2)$$

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

359

360 **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
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

361 ^{*}MT data not available on September 5 and 19.

362 ^{**}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 **horizontal** wind shift (not shown here). **A rapid decrease was found in CS, which represents the rate of condensation of low-volatile vapors onto the existing aerosol particles (Dada et al., 2017), implying that the aerosol population also altered.** 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.

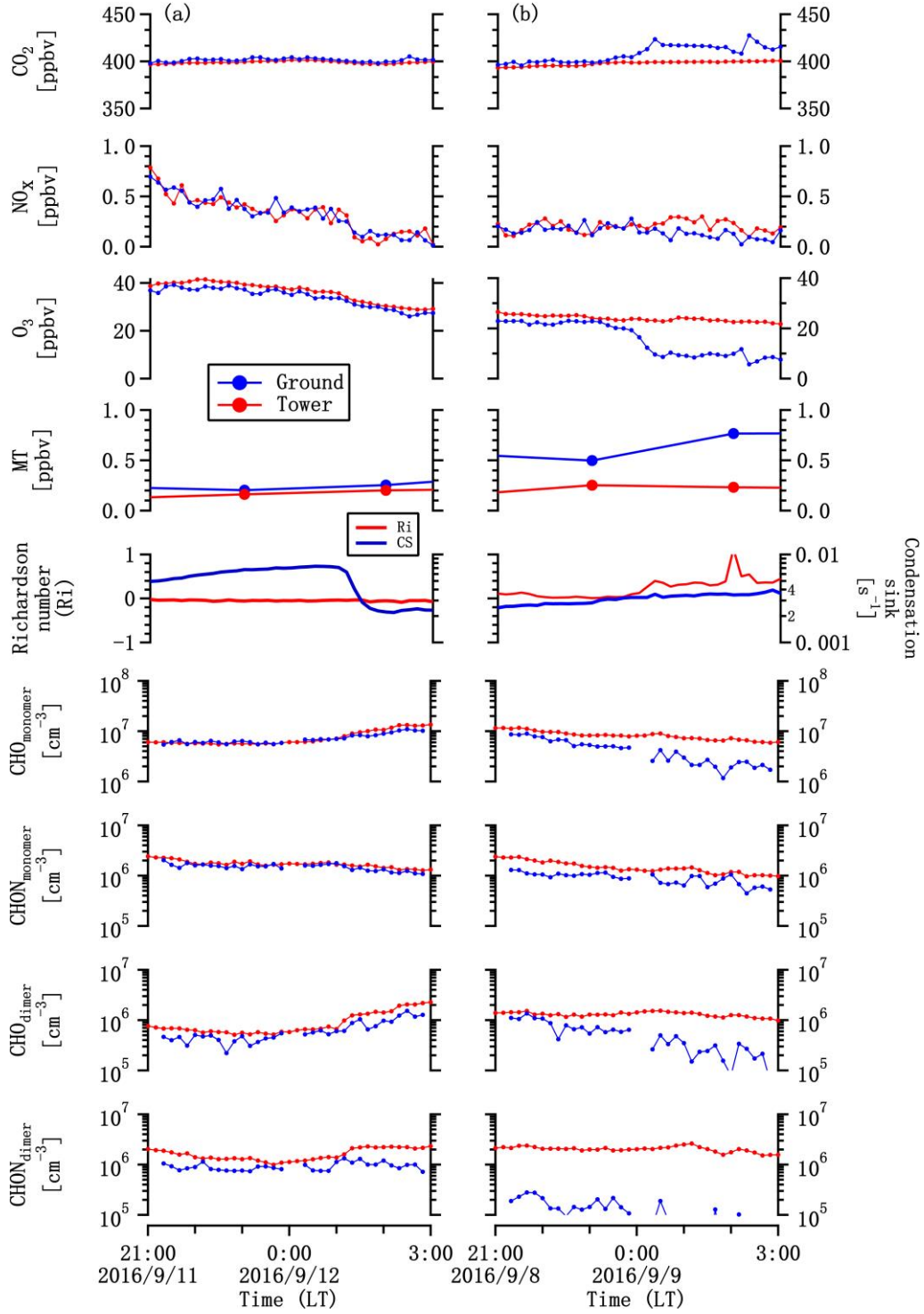


Figure 5 (a) Time series of ground and tower concentrations of CO_2 , NO_x , O_3 , MT, and selected HOM groups in the selected “non-inversion night” (September 11), and (b) “inversion night” (September 8). Ri is calculated with the meteorology data of ground and tower levels. CS is determined based on the aerosol data measured at 8 m above ground level.

The ground O_3 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, **despite the CS (generally the main sink for HOM in the atmosphere) staying practically constant.** 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.

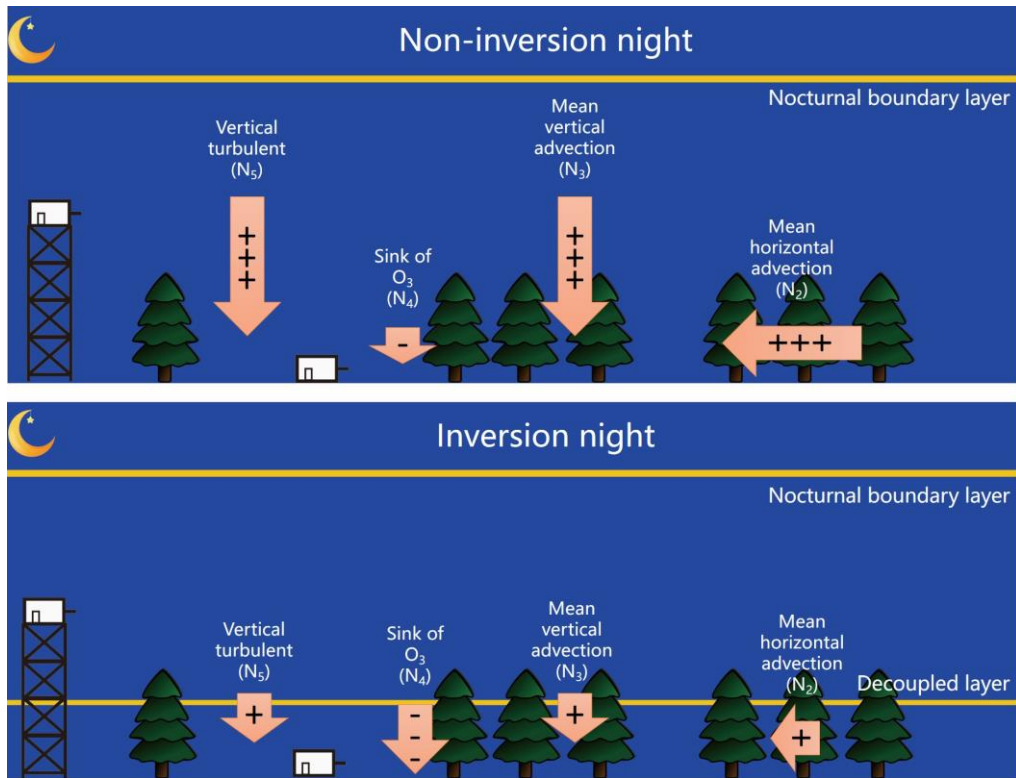


Figure 6 Schematic figure showing how vertical mixing, vertical advection, and horizontal advection influence ground O_3 concentrations differently in non-inversion night and inversion night at SMEAR II station.

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 .

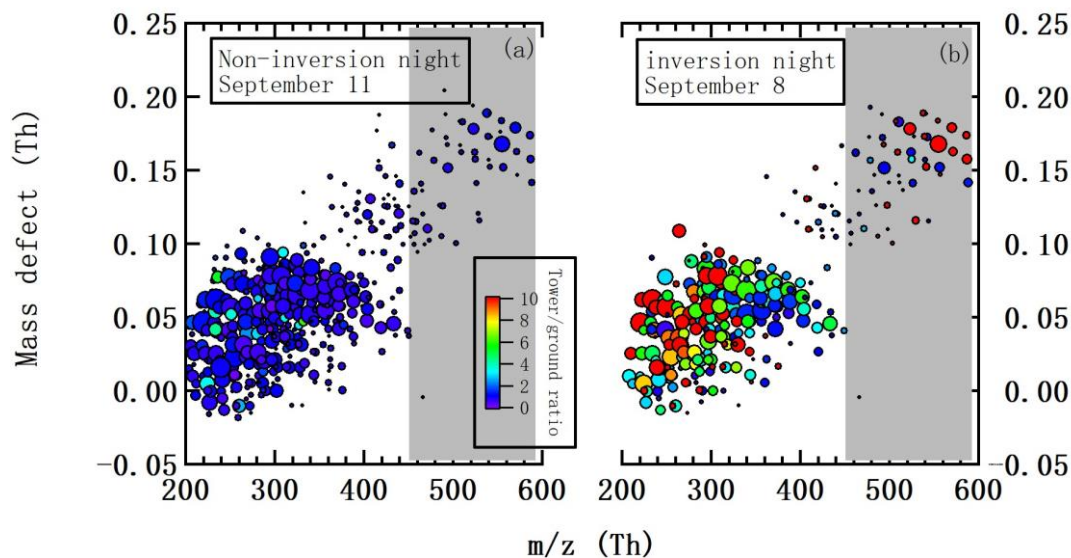


Figure 7 Mass defect (MD) plots of the selected (a) “non-inversion night” case (September 11), and (b) “inversion night” case (September 8). Color code indicates the ratios between tower/ground HOM concentrations. Grey shade area denotes the dimer range (m/z 450-600).

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 (Figure 7) separates all identified compounds according to their exact masses on the x-axis and the deviation from the integer mass on the y-axis. Each circle represents a compound, with the areas scaled by concentrations, and colored by the ratios between tower and ground concentrations. Figure 7a and 7b are MD plots showing the mean spectra of the selected non-inversion night (September 11) and inversion night (September 8). Without the formation of a decoupled layer, nearly the same concentration distributions of HOMs were observed. In contrast, during the inversion night (September 8, Figure 7b), 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.

4.4 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.

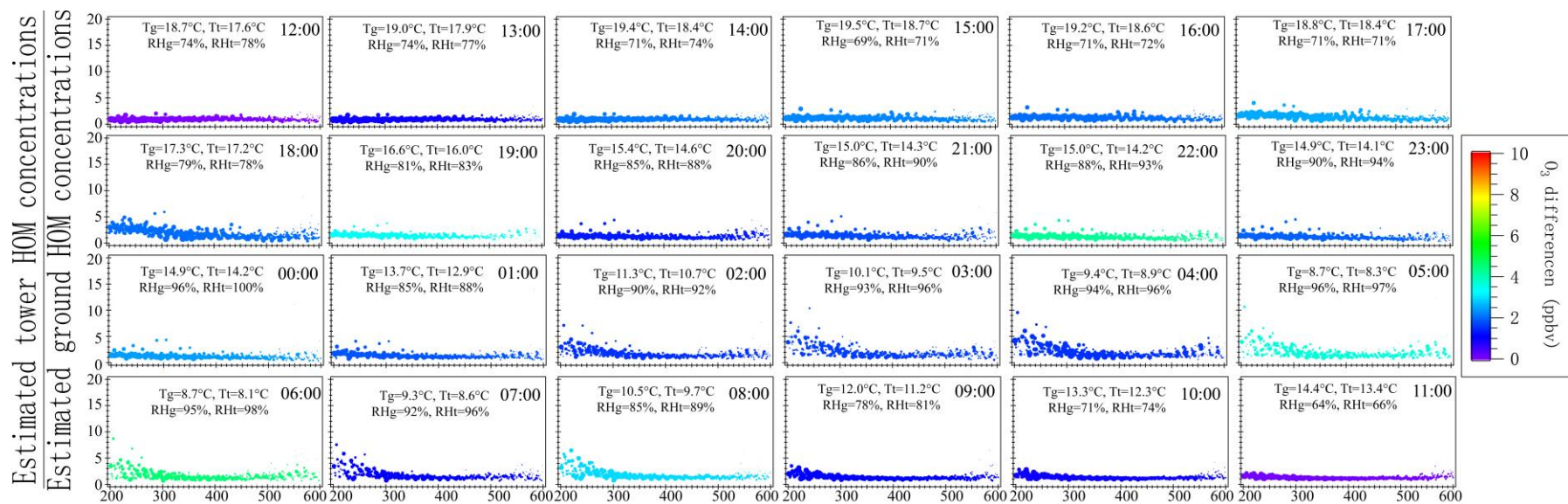


Figure 8 Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 11, 12:00 to September 12, 11:00 (non-inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3,tower} - O_{3,ground}$). Hourly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

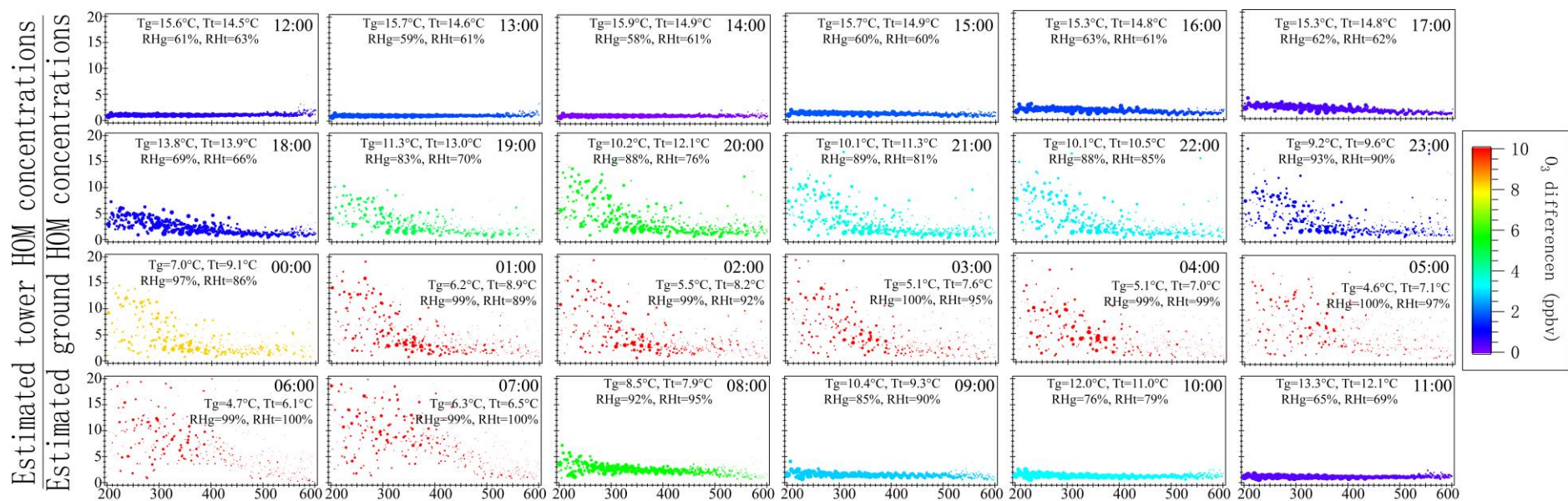


Figure 9 Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 8, 12:00 to September 9, 11:00 (inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3\text{tower}} - O_{3\text{ground}}$). 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 %, respectively),
335 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 **5 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 **at this**
381 **site** might not be representative for the entire nocturnal boundary layer. Conventionally,
382 field measurements of HOMs and other parameters are mostly performed close to the
383 ground, and the **possible** effect of boundary layer dynamics and micrometeorological
384 processes to the HOM concentrations have rarely been considered. Aerosol particle
385 growth and SOA formation rates at ground level are likely to be influenced by the
386 reduced HOM concentrations in the inversion nights. **However, there are still**
387 **limitations due to current experiment design, such as horizontal separation in**
388 **instrument set-up, or the uncertainties from using point measurements at two heights to**
389 **infer larger scale exchange.** Clearly, more vertical and planar measurements of HOMs
390 are needed to confirm the emerging picture presented here. Influence of boundary layer
391 dynamics should be better characterized and evaluated in future field campaigns.

392

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404

405 Reference:

406 Aalto, P., Hämeri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J. M., Hoell, C., O’
407 C. D., Hansson, H.-C., Väkevä, M., Koponen, I. K., Buzorius, G. and Kulmala, M.:
408 Physical characterization of aerosol particles during nucleation events, *Tellus B Chem.*
409 *Phys. Meteorol.*, 53(4), 344–358, doi:10.3402/tellusb.v53i4.17127, 2001.

410 Alekseychik, P., Mammarella, I., Launiainen, S., Rannik, Ü. and Vesala, T.: Evolution
411 of the nocturnal decoupled layer in a pine forest canopy, *Agric. For. Meteorol.*, 174, 15–
412 27, doi:10.1016/j.agrformet.2013.01.011, 2013.

413 Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q. and Boy, M.: Chemodiversity of
414 a Scots pine stand and implications for terpene air concentrations, *Biogeosciences*, 9(2),
415 689–702, doi:10.5194/bg-9-689-2012, 2012.

416 Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M. and Hansel,
417 A.: Accretion Product Formation from Self- and Cross-Reactions of RO₂ Radicals in
418 the Atmosphere, *Angew. Chemie Int. Ed.*, 57(14), 3820–3824,
419 doi:10.1002/anie.201710989, 2018.

420 Bianchi, F., Tröstl, J., Junninen, H., Frege, C., Henne, S., Hoyle, C. R., Molteni, U.,
421 Herrmann, E., Adamov, A., Bukowiecki, N., Chen, X., Duplissy, J., Gysel, M., Hutterli,
422 M., Kangasluoma, J., Kontkanen, J., Kürten, A., Manninen, H. E., Münch, S., Peräkylä,
423 O., Petäjä, T., Rondo, L., Williamson, C., Weingartner, E., Curtius, J., Worsnop, D. R.,
424 Kulmala, M., Dommen, J. and Baltensperger, U.: New particle formation in the free
425 troposphere: A question of chemistry and timing., *Science*, 352(6289), 1109–12,
426 doi:10.1126/science.aad5456, 2016.

427 Bianchi, F., Garmash, O., He, X., Yan, C., Iyer, S., Rosendahl, I., Xu, Z., Rissanen, M.

428 P., Riva, M., Taipale, R., Sarnela, N., Petäjä, T., Worsnop, D. R., Kulmala, M., Ehn, M.
429 and Junninen, H.: The role of highly oxygenated molecules (HOMs) in determining the
430 composition of ambient ions in the boreal forest, *Atmos. Chem. Phys.*, 17(22), 13819–
431 13831, doi:10.5194/acp-17-13819-2017, 2017.

432 Chen, X., Quéléver, L. L. J., Fung, P. L., Kesti, J., Rissanen, M. P., Bäck, J., Keronen,
433 P., Junninen, H., Petäjä, T., Kerminen, V.-M. and Kulmala, M.: Observations of ozone
434 depletion events in a Finnish boreal forest, *Atmos. Chem. Phys.*, 18(1), 49–63,
435 doi:10.5194/acp-18-49-2018, 2018.

436 Crouse, J. D., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G. and Wennberg, P. O.:
437 Autoxidation of Organic Compounds in the Atmosphere, *J. Phys. Chem. Lett.*, 4(20),
438 3513–3520, doi:10.1021/jz4019207, 2013.

439 Dada, L., Paasonen, P., Nieminen, T., Mazon, S. B., Kontkanen, J., Peräkylä, O.,
440 Lehtipalo, K., Hussein, T., Petäjä, T., Kerminen, V.-M., Bäck, J. and Kulmala, M.:
441 Long-term analysis of clear-sky new particle formation events and nonevents in
442 Hyytiälä, *Atmos. Chem. Phys.*, 17, 6227–6241, doi:10.5194/acp-17-6227-2017, 2017.

443 Eerdekens, G., Yassaa, N., Sinha, V., Aalto, P. P., Aufmhoff, H., Arnold, F., Fiedler, V.,
444 Kulmala, M. and Williams, J.: VOC measurements within a boreal forest during spring
445 2005: on the occurrence of elevated monoterpene concentrations during night time
446 intense particle concentration events, *Atmos. Chem. Phys.*, 9(21), 8331–8350,
447 doi:10.5194/acp-9-8331-2009, 2009.

448 Ehn, M., Junninen, H., Petäjä, T., Kurtén, T., Kerminen, V.-M., Schobesberger, S.,
449 Manninen, H. E., Ortega, I. K., Vehkamäki, H., Kulmala, M. and Worsnop, D. R.:
450 Composition and temporal behavior of ambient ions in the boreal forest, *Atmos. Chem.*
451 *Phys.*, 10(17), 8513–8530, doi:10.5194/acp-10-8513-2010, 2010.

452 Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Dal Maso,
453 M., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J. and Mentel, T.
454 F.: Gas phase formation of extremely oxidized pinene reaction products in chamber and
455 ambient air, *Atmos. Chem. Phys.*, 12(11), 5113–5127, doi:10.5194/acp-12-5113-2012,

456 2012.

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

464 Ehn, M., Berndt, T., Wildt, J. and Mentel, T.: Highly Oxygenated Molecules from
465 Atmospheric Autoxidation of Hydrocarbons: A Prominent Challenge for Chemical
466 Kinetics Studies, *Int. J. Chem. Kinet.*, 49(11), 821–831, doi:10.1002/kin.21130, 2017.

467 Hari, P., Nikinmaa, E., Pohja, T., Siivola, E., Bäck, J., Vesala, T. and Kulmala, M.:
468 Station for measuring ecosystem-atmosphere relations: SMEAR, *Phys. Physiol. For.*
469 *Ecol.*, 9789400756, 471–487, doi:10.1007/978-94-007-5603-8_9, 2013.

470 Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A. and Curtius,
471 J.: Characterization of the mass-dependent transmission efficiency of a CIMS, *Atmos.*
472 *Meas. Tech.*, 9(4), 1449–1460, doi:10.5194/amt-9-1449-2016, 2016.

473 Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin,
474 R. L., Kulmala, M. and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster
475 measurements using CI-API-TOF, *Atmos. Chem. Phys.*, 12(9), 4117–4125,
476 doi:10.5194/acp-12-4117-2012, 2012.

477 Jokinen, T., Sipilä, M., Richters, S., Kerminen, V.-M., Paasonen, P., Stratmann, F.,
478 Worsnop, D., Kulmala, M., Ehn, M., Herrmann, H. and Berndt, T.: Rapid Autoxidation
479 Forms Highly Oxidized RO₂ Radicals in the Atmosphere, *Angew. Chemie Int. Ed.*,
480 53(52), 14596–14600, doi:10.1002/anie.201408566, 2014.

481 Jokinen, T., Kausiala, O., Garmash, O., Peräkylä, O., Junninen, H., Schobesberger, S.,
482 Yan, C., Sipilä, M. and Rissanen, M. P.: Production of highly oxidized organic
483 compounds from ozonolysis of β-caryophyllene: laboratory and field measurements,

484 Boreal Env. Res, 21, 262–273, 2016.

485 Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostianen, R., Rohner,
486 U., Gonin, M., Fuhrer, K., Kulmala, M. and Worsnop, D. R.: A high-resolution mass
487 spectrometer to measure atmospheric ion composition, *Atmos. Meas. Tech.*, 3(4), 1039–
488 1053, doi:10.5194/amt-3-1039-2010, 2010.

489 Katul, G. G., Finnigan, J. J., Poggi, D., Leuning, R. and Belcher, S. E.: The Influence
490 of Hilly Terrain on Canopy-Atmosphere Carbon Dioxide Exchange, *Boundary-Layer
491 Meteorol.*, 118(1), 189–216, doi:10.1007/s10546-005-6436-2, 2006.

492 Katul, G. G., Porporato, A., Shah, S. and Bou-Zeid, E.: Two phenomenological
493 constants explain similarity laws in stably stratified turbulence, *Phys. Rev. E*, 89(2),
494 023007, doi:10.1103/PhysRevE.89.023007, 2014.

495 Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi,
496 M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R.,
497 Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke,
498 S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C.,
499 Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim,
500 J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S.,
501 Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K.,
502 Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N.,
503 Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y.,
504 Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E.,
505 Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen,
506 J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S.
507 and Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533(7604),
508 521–526, doi:10.1038/nature17953, 2016.

509 Kulmala, L., Launiainen, S., Pumpanen, J., Lankreijer, H., Lindroth, A., Hari, P. and
510 Vesala, T.: H₂O and CO₂ fluxes at the floor of a boreal pine forest, *Tellus, Ser. B Chem.
511 Phys. Meteorol.*, 60 B(2), 167–178, doi:10.1111/j.1600-0889.2007.00327.x, 2008.

512 Kulmala, M., Dal Maso, M., Mäkelä, J. M., Pirjola, L., Väkevä, M., Aalto, P.,
513 Miikkulainen, P., Hämeri, K. and O'Dowd, C. D.: On the formation, growth and
514 composition of nucleation mode particles, *Tellus, Ser. B Chem. Phys. Meteorol.*, 53(4),
515 479–490, doi:10.3402/tellusb.v53i4.16622, 2001.

516 Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen,
517 T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T.,
518 Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä,
519 J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L.,
520 Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston,
521 M. V, Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen,
522 V.-M. and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation.,
523 *Science*, 339(6122), 943–6, doi:10.1126/science.1227385, 2013.

524 Kürten, A., Bergen, A., Heinritzi, M., Leiminger, M., Lorenz, V., Piel, F., Simon, M.,
525 Sitals, R., Wagner, A. C. and Curtius, J.: Observation of new particle formation and
526 measurement of sulfuric acid, ammonia, amines and highly oxidized organic molecules
527 at a rural site in central Germany, *Atmos. Chem. Phys.*, 16, 12793–12813,
528 doi:10.5194/acp-16-12793-2016, 2016.

529 Launiainen, S., Katul, G. G., Grönholm, T. and Vesala, T.: Partitioning ozone fluxes
530 between canopy and forest floor by measurements and a multi-layer model, *Agric. For.*
531 *Meteorol.*, 173, 85–99, doi:10.1016/j.agrformet.2012.12.009, 2013.

532 Lauros, J., Nilsson, E. D., Dal Maso, M. and Kulmala, M.: Contribution of mixing in
533 the ABL to new particle formation based on observations, *Atmos. Chem. Phys.*, 7(18),
534 4781–4792, doi:10.5194/acp-7-4781-2007, 2007.

535 Mahrt, L.: Nocturnal Boundary-Layer Regimes, *Boundary-Layer Meteorol.*, 88(2),
536 255–278, doi:10.1023/A:1001171313493, 1998.

537 Mahrt, L., Vickers, D., Nakamura, R., Soler, M. R., Sun, J., Burns, S. and Lenschow, D.
538 H.: Shallow Drainage Flows, *Boundary-Layer Meteorol.*, 101(2), 243–260,
539 doi:10.1023/A:1019273314378, 2001.

540 Mammarella, I., Kolari, P., Rinne, J., Keronen, P., Pumpanen, J. and Vesala, T.:
541 Determining the contribution of vertical advection to the net ecosystem exchange at
542 Hyytiälä forest, Finland, *Tellus B Chem. Phys. Meteorol.*, 59(5), 900–909,
543 doi:10.1111/j.1600-0889.2007.00306.x, 2007.

544 Mentel, T. F., Springer, M., Ehn, M., Kleist, E., Pullinen, I., Kurtén, T., Rissanen, M.,
545 Wahner, A. and Wildt, J.: Formation of highly oxidized multifunctional compounds:
546 autoxidation of peroxy radicals formed in the ozonolysis of alkenes—deduced from
547 structure–product relationships, *Atmos. Chem. Phys. Discuss.*, 15(2), 2791–2851, 2015.

548 Orlando, J. J. and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry:
549 an overview with emphasis on recent issues of atmospheric significance, *Chem. Soc.*
550 *Rev.*, 41(19), 6294, doi:10.1039/c2cs35166h, 2012.

551 Ouwersloot, H. G., Vilà-Guerau de Arellano, J., Nölscher, A. C., Krol, M. C., Ganzeveld,
552 L. N., Breitenberger, C., Mammarella, I., Williams, J. and Lelieveld, J.:
553 Characterization of a boreal convective boundary layer and its impact on atmospheric
554 chemistry during HUMPPA-COPEC-2010, *Atmos. Chem. Phys.*, 12(19), 9335–9353,
555 doi:10.5194/acp-12-9335-2012, 2012.

556 Rannik, Ü., Mammarella, I., Keronen, P. and Vesala, T.: Vertical advection and
557 nocturnal deposition of ozone over a boreal pine forest, *Atmos. Chem. Phys.*, 9(6),
558 2089–2095, doi:10.5194/acp-9-2089-2009, 2009.

559 Rannik, Ü., Altimir, N., Mammarella, I., Bäck, J., Rinne, J., Ruuskanen, T. M., Hari, P.,
560 Vesala, T. and Kulmala, M.: Ozone deposition into a boreal forest over a decade of
561 observations: evaluating deposition partitioning and driving variables, *Atmos. Chem.*
562 *Phys.*, 12(24), 12165–12182, doi:10.5194/acp-12-12165-2012, 2012.

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

567 Raupach, M. R. and Thom, A. S.: Turbulence in and above Plant Canopies, *Annu. Rev.*

568 Fluid Mech., 13(1), 97–129, doi:10.1146/annurev.fl.13.010181.000525, 1981.

569 Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kangasluoma, J., Sarnela, N.,
570 Junninen, H., Jørgensen, S., Schallhart, S., Kajos, M. K., Taipale, R., Springer, M.,
571 Mentel, T. F., Ruuskanen, T., Petäjä, T., Worsnop, D. R., Kjaergaard, H. G. and Ehn, M.:
572 The Formation of Highly Oxidized Multifunctional Products in the Ozonolysis of
573 Cyclohexene, *J. Am. Chem. Soc.*, 136(44), 15596–15606, doi:10.1021/ja507146s, 2014.

574 Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T. and
575 Kulmala, M.: Technical Note: Quantitative long-term measurements of VOC
576 concentrations by PTR-MS - measurement, calibration, and volume mixing ratio
577 calculation methods, *Atmos. Chem. Phys.*, 8(22), 6681–6698, doi:10.5194/acp-8-6681-
578 2008, 2008.

579 Tröstl, J., Chuang, W. K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L.,
580 Frege, C., Bianchi, F., Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven,
581 J. S., Duplissy, J., Adamov, A., Almeida, J., Bernhammer, A.-K., Breitenlechner, M.,
582 Brilke, S., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Gysel,
583 M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H.,
584 Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lawler, M., Leiminger, M., Mathot, S.,
585 Möhler, O., Nieminen, T., Onnela, A., Petäjä, T., Piel, F. M., Miettinen, P., Rissanen, M.
586 P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Sipilä, M., Smith, J. N.,
587 Steiner, G., Tomè, A., Virtanen, A., Wagner, A. C., Weingartner, E., Wimmer, D.,
588 Winkler, P. M., Ye, P., Carslaw, K. S., Curtius, J., Dommen, J., Kirkby, J., Kulmala, M.,
589 Riipinen, I., Worsnop, D. R., Donahue, N. M. and Baltensperger, U.: The role of low-
590 volatility organic compounds in initial particle growth in the atmosphere, *Nature*,
591 533(7604), 527–531, doi:10.1038/nature18271, 2016.

592 Vickers, D., Irvine, J., Martin, J. G. and Law, B. E.: Nocturnal subcanopy flow regimes
593 and missing carbon dioxide, *Agric. For. Meteorol.*, 152(1), 101–108,
594 doi:10.1016/j.agrformet.2011.09.004, 2012.

595 Viggiano, A. A., Seeley, J. V., Mundis, P. L., Williamson, J. S. and Morris, R. A.: Rate

596 Constants for the Reactions of $\text{XO}_3\text{-(H}_2\text{O)}_n$ ($\text{X} = \text{C, HC, and N}$) and $\text{NO}_3\text{-(HNO}_3)_n$ with
597 H_2SO_4 : Implications for Atmospheric Detection of H_2SO_4 , *J. Phys. Chem. A*, 101(44),
598 8275–8278, doi:10.1021/jp971768h, 1997.

599 Yan, C., Nie, W., Äijälä, M., Rissanen, M. P., Canagaratna, M. R., Massoli, P., Junninen,
600 H., Jokinen, T., Sarnela, N., Häme, S. A. K., Schobesberger, S., Canonaco, F., Yao, L.,
601 Prévôt, A. S. H., Petäjä, T., Kulmala, M., Sipilä, M., Worsnop, D. R. and Ehn, M.:
602 Source characterization of highly oxidized multifunctional compounds in a boreal
603 forest environment using positive matrix factorization, *Atmos. Chem. Phys.*, 16(19),
604 12715–12731, doi:10.5194/acp-16-12715-2016, 2016.

605 Zhao, J., Ortega, J., Chen, M., McMurry, P. H. and Smith, J. N.: Dependence of particle
606 nucleation and growth on high-molecular-weight gas-phase products during ozonolysis
607 of α -pinene, *Atmos. Chem. Phys.*, 13(15), 7631–7644, doi:10.5194/acp-13-7631-2013,
608 2013.

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