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.
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.
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: HNO$_3$*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 (Hyttinen 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 HOM*NO$_3$- clusters are thermodynamically extremely stable (Hyttinen 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 ~6.5 m²m⁻², a stand density of ~1400 trees ha⁻¹, and an average diameter at breast height (DBH) of ~0.16 m (Bäck et al., 2012; Launiainen et al., 2013). The forest floor is majorly covered with a shallow dwarf shrub (a LAI of ~0.5 m²m⁻²) and moss layer (a LAI of ~1 m²m⁻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 $\sim26\%$ 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 (total HOM in tower) / (total HOM at ground) = ~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 (R² = 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. Monoterpenes emissions (which are HOM precursors) have a strong temperature dependence, and therefore the higher temperature show higher HOM concentrations (at both heights).
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:*

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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.](image_url)

*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:*


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
formation of a shallow decoupled layer below the canopy. Near ground HOMs were influenced by the changes in the precursors and oxidants, and enhancement of the loss on surfaces in this layer, while the HOMs above the canopy top were not significantly affected. 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. This could, in turn, influence the growth of newly formed particles and SOA formation below the canopy where a large majority of measurements are typically conducted.

2 Introduction

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

The direct observation of HOMs has only recently become possible, following the developments of the Atmospheric-Pressure-interface Time-Of-Flight (API-TOF, measures the charged HOM clusters) (Junninen et al., 2010) and Chemical Ionization Atmospheric-Pressure-interface Time-Of-Flight (CI-API-TOF, measures the neutral HOM molecules) (Jokinen et al., 2012) mass spectrometers. Ehn et al. (2010) and Bianchi et al. (2017) found that the naturally charged HOM clusters could be observed
every night in boreal forest during spring. Out of the observed ambient mass spectra, a
significant part could be reproduced in a chamber by introducing the monoterpenes α-
pinene (C_{10}H_{16}, the major biogenic VOC in the boreal forest) and ozone (O_{3}) (Ehn et
al., 2012).

Further investigations of HOM formation chemistry have been done in both laboratory
and field studies. Based on current understanding from laboratory experiments, the
formation of HOM molecules involves three main steps: 1) initial formation of peroxyl
radicals (RO_{2}) from VOC oxidation; 2) RO_{2} auto-oxidation, that is, the isomerization
of the RO_{2} via intramolecular H-shifts and the subsequent oxygen (O_{2}) additions; and
3) radical termination, forming closed-shell molecules (Crounse et al., 2013; Ehn et al.,
2014; Jokinen et al., 2014, 2016; Rissanen et al., 2014; Mentel et al., 2015). In the
atmosphere, HOM formation studies are complicated by the plethora of different
compounds and processes taking place. However, recent ambient measurements
together with factor analysis were able to shed light on the HOM formation pathways
in the boreal forest (Yan et al., 2016). They showed that the majority of the daytime
production of HOMs was from reactions initiated by the oxidation of monoterpenes
(MT) with hydroxyl radical (OH) or O_{3}. The RO_{2} after auto-oxidation was either
terminated by hydroperoxyl radical (HO_{2}) or self-termination (Orlando and Tyndall,
2012), to form a non-nitrate HOM monomer (CHO_{monomer}, mainly C_{9} and C_{10}
compounds, with masses between 290-450 Th after clustering with the charging ion
(NO_{3}^{+}) of the instrument); or reacting with nitrogen oxides (NO_{x}) to form an
organonitrate HOM monomer (CHON_{monomer}). During nighttime, MT were mainly
oxidized by O_{3} and NO_{3} radical. Furthermore, due to the lower nocturnal HO_{2} and NO_{x}
concentrations, besides the production of CHON_{monomer}, the RO_{2} products could also
react with another RO_{2} to form a non-nitrate HOM dimer (CHO_{dimer}, mainly C_{16-20}
compounds, with masses between 450-600 Th after clustering with NO_{3}^{+}) or an
organonitrate HOM dimer (CHON_{dimer}), depending on the oxidants of the RO_{2} radical.
Beyond those chemical pathways, varied meteorological conditions are also factors influencing the MT and oxidants at different heights above the forest floor. Unsurprisingly, the oxidants producing HOMs (e.g. \(O_3\)) were found almost uniformly distributed within the well-mixed daytime boundary layer (Chen et al., 2018). In contrast, the nocturnal boundary layer was shallow with stability regimes that depended on radiative cooling within the canopy and turbulent shear stresses at the canopy top. In Hyytiälä, the depletions of \(O_3\) below the canopy were frequently observed during nighttime, while the \(O_3\) above the canopy was less affected. The MT concentration at ground level increased when \(O_3\) was depleted (Eerdekens et al., 2009). The inhomogeneous distribution of the precursors and oxidants below and above the canopy might further impact nocturnal HOM distributions, which frames the scope of this study. Until now, all CI-API-TOF deployments have been at ground level, and the main subject of inquiry here is the vertical information on HOMs and the role of meteorological condition in shaping them. A characterization of the HOMs at different heights provides a decisive advantage in disentangling the role of non-uniform mixing within the atmospheric layers impacted by strong thermal stratification, especially inside the canopy volume.

The first measurements of the HOM concentrations at two different heights (36 m and 1.5 m a.g.l.) during September 2016 are presented and discussed. The influence of boundary layer dynamics on the HOMs at these different heights at SMEAR II station are analyzed and characterized in conjunction with auxiliary turbulence and micrometeorological measurements.
3 Experimental

3.1 Measurement site description

The measurements were performed at the SMEAR II station (Station for Measuring Ecosystem–Atmosphere Relations) in the boreal forest in Hyytiälä, southern Finland (61°51' N, 24°17' E, 181 m a.s.l., Hari and Kulmala, 2005; Hari et al., 2013) during September 2016. There is no large anthropogenic emission source at or near the site. The closest sources are the two sawmills ~5 km southeast of the site, and from the city area of Tampere (~60 km away). The forest surrounding the station is primarily Scots pine with a mean canopy height of ~17.5 m, a total leaf area index (LAI) of ~6.5 m²m⁻², a stand density of ~1400 trees ha⁻¹, and an average diameter at breast height (DBH) of ~0.16 m (Bäck et al., 2012; Launiainen et al., 2013). The forest floor is majorly covered with a shallow dwarf shrub (a LAI of ~0.5 m²m⁻²) and moss layer (a LAI of ~1 m²m⁻²) (Kulmala et al., 2008; Launiainen et al., 2013). The planetary boundary layer height at the SMEAR II station has been determined from previous studies using radiosondes (Lauros et al., 2007; Ouwersloot et al., 2012) and balloon soundings (Eerdekens et al., 2009). Roughly, these heights span some 400 m (March) to 1700 m (August) at noontime, and 100 m (March) to <160 m (April) at midnight.

3.2 Instrumentation

Concentration of HOM molecules were measured with two nitrate-ion based CI-APi-TOF mass spectrometers. The CI-APi-TOF measuring at higher altitude was deployed at the top of a 35 m tower located ~20 m horizontally from the ground measurement location. Both instruments were working in rooms with air-conditioning and room temperatures controlled at 25 °C. The inlets of the two instruments were pointed to the southeast direction and fixed at ~36 m and ~1.5 m above ground. The tower measurement is about twice the canopy height, which is still within the roughness sublayer of the forest (Raupach and Thom, 1981). The instrument setup of the two CI-
API-TOF mass spectrometers were similar. In brief, the CI-API-TOF was the combination of a chemical ionization (CI) inlet, and an atmospheric pressure interface time-of-flight (API-TOF) mass spectrometer (Aerodyne Research Inc., USA, and Tofwerk AG, Switzerland). The ambient air was first drawn into the inlet with a sample flow of 7 lpm (liter per minute), and then centered to an ion reaction tube surrounded by sheath flow (filtered air, 35 lpm). Meanwhile, the nitrate ions carried by the sheath gas, which were generated by exposing the nitric acid (HNO₃) to soft x-ray radiation, were guided into the sample gas by an electrical field at ambient pressure (~100 ms reaction time). Neutral molecules (M) in the sample air were ionized by either clustering with charged nitrate/nitric acid ((HNO₃)ₙ₋₀.2·NO₃⁻) to form (M)·NO₃⁻ cluster ions, or losing a proton to the charging ions to form deprotonated ions (e.g., H₂SO₄·NO₃⁻→HSO₄⁻+HNO₃). The ions then entered the API part, which was a three-stage vacuum chamber, through a pinhole. In the API, two quadrupoles and stack of ion lenses guide the ions into the TOF mass spectrometer, where ions were separated based on their mass-to-charge (m/z) ratios. A more detailed description of this instrument has been given by Junninen et al. (2010) and Jokinen et al. (2012). Mass spectra obtained from the instrument were analyzed using the ‘tofTools’ program described in Junninen et al. (2010). Determination of the concentration of a measured molecule M was based on the following equation:

\[ [M] = \frac{\sum M}{\sum \text{reagent ion count rates}} \times C \]  

(1)

where the sum of ion count rates was an inclusion of all detected ions relating to compound M, whether deprotonated or in clusters with reagent ions, and the sum of reagent ion count rates is the total signal of the charged nitric acid ions. C was the calibration coefficient, which was assigned the same value for all detected compounds. This assignment is only valid for compounds that cluster with the reagent ions at the collision limit, such as H₂SO₄ (Viggiano et al., 1997) and have equal collision rates. The collision rates of nitrate ions with H₂SO₄ and with HOMs are expected to be very close (Ehn et al., 2014). Here, a calibration coefficient of 1 \times 10^{10} \text{molec cm}^{-3}, estimated...
from previous calibrations with similar settings using sulfuric acid and theoretical constraints (Ehn et al., 2014), with 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. However, the comparability of the two CI-APi-TOF instruments is of great importance, and results cannot be allowed to vary e.g. as a result of inevitable differences in the mass-dependent transmission efficiency (TE). For a detailed discussion on factors affecting the TE of a CI-APi-TOF, we refer to Heinritzi et al. (2016). To this end, instead of directly evaluating the TE of each instrument, a “relative” TE of the two CI-APi-TOFs was used for data correction: we selected a time period at noon-time on September 9 with well-mixed boundary layer condition, identified with the clear and sunny weather and homogeneous vertical distribution of monoterpene and other trace gases., and assumed the HOM concentrations at the two heights to be the same. Thus, the relative TE was obtained from the concentration ratio between the two CI-APi-TOFs at each m/z (Figure 1). 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. Weaker correlation was obtained in the 200-250 and 500-600 Th mass ranges, but in the mass range where most of the HOMs were located (290-500 Th) there is very little scatter around the fitted curve, clearly suggesting that observed differences in the two instruments responses were mainly due to differences in TE. 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). Additionally, an inter-comparison between the two
instruments with a permeation tube containing trinitrotriazinane (C₃H₆N₆O₆) 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. Finally, it should be noted that the difference in TE between the two instruments was larger than one would normally expect, since the tower CI-API-TOF had been tuned for higher sensitivity at the largest masses (at the expense of transmission at the lower masses).

Figure 1 The relative TE curve between the two CI-API-TOF mass spectrometers. Inter-comparison results using a permeation tube containing trinitrotriazinane (C₃H₆N₆O₆) are shown in red circles.

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.

The MT, trace gases, and meteorological parameters were continuously monitored at the different heights (4.2 m, 8.4 m, 16.8 m, 33.6 m, 50.4 m, 67.2 m, 101 m, and 125 m) on a 126 m mast ~100 m away from the location of the CI-API-TOFs. The data at 4.2
m and 33.6 m were used in this study to represent the concentrations at near ground and
tower level, respectively. Ambient MT concentration was measured every third hour
using a proton transfer reaction mass spectrometer with a lower detection limit of 1
pptv (PTR-MS, Ionicon Analytik GmbH; Taipale et al., 2008). The O₃ concentration
was measured with an UV light absorption analyzer that had a lower detection limit of
1 ppbv (TEI model 49C, Thermo Fisher Scientific, USA). The NOₓ measurement was
conducted using a chemiluminescence analyzer (TEI model 42C TL, Thermo Fisher
Scientific, USA). The lower detection limit of the NOₓ analyzer is 100 pptv. The CO₂
measurement was performed using an infrared detection system (LI-840, LiCor
Biosciences, Lincoln, NE, USA). The aerosol number concentration size distributions
were obtained with a twin differential mobility particle sizer (twin-DMPS) for the size
range from 3-1000 nm (Aalto et al., 2001) at 8 m height above ground, and was used to
calculate condensation sink (CS) based on the method from Kulmala et al. (2001). Air
temperature was measured with PT-100 resistance thermometers. Air relative humidity
(RH) was measured with RH sensors (Rotronic Hygromet model MP102H with
Hygroclip HC2-S3, Rotronic AG, Switzerland). Global radiation (solar radiation in
wavelength range of 0.3-4.8 µm) was obtained with a Pyranometer (Reemann TP3,
Astrodata, Estonia) above the canopy top at 18 m. All the data presented are at 10 min
averaging intervals, except for the MT (in 1-hour averaging interval). A schematic
figure showing locations of all the measured parameters is provided in Figure S2.

4 Results and discussion

4.1 Data overview

The Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget
(IBAIRN) campaign was conducted from September 1 to 25, 2016. After data quality
checks, only the measurements collected after September 5 were used. Figure 2 shows
the overall time series of the meteorological parameters measured at ground and tower
levels, including the temperature, RH, global radiation, concentrations of trace gases, MT, and total HOMs. The weather was generally sunny and clear during the campaign except for a few cloudy (September 10, 15, and 22-23) and drizzling (September 24 and 25) days. The mean air temperature and RH observed at ground level were $10.8 \pm 3.3 \degree C$ and $87 \pm 13 \%$ (1σ standard deviation), and at the tower level were $10.5 \pm 3.0 \degree C$ and $88 \pm 14 \%$, respectively. The O$_3$ concentrations measured at ground and tower levels were $21 \pm 8$ ppbv and $25 \pm 6$ ppbv, respectively. The air temperature, RH and O$_3$ measured at the two heights were close to each other during daytime. The NO$_x$ concentrations were quite low throughout the campaign, the mean NO$_x$ concentrations were mostly around the reported detection limit at $0.4 \pm 0.4$ ppbv (ground) and $0.4 \pm 0.5$ ppbv (tower), yet showed an overall good agreement between the measurements at the different heights. The MT concentrations at ground level ($0.38 \pm 0.34$ ppbv on average) were generally higher than that above the canopy level ($0.20 \pm 0.16$ ppbv).
Figure 2 The overall time series of the measured trace gases, meteorological parameters and estimated total HOM concentrations at the ground (blue) and tower (red) levels.

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

4.2 Inter-comparison of estimated total HOM concentrations

The estimated total HOM concentrations at the two heights were not different during the day (mean ± 1σ standard deviation and median concentrations of $4.1 \pm 2.3 \times 10^8$ cm$^{-3}$ and $3.6 \times 10^8$ cm$^{-3}$ at ground level, $4.3 \pm 2.6 \times 10^8$ cm$^{-3}$ and $4.0 \times 10^8$ cm$^{-3}$ at tower level), which validates the use of only one day of data for scaling the TE of the ground CI-API-TOF to match the HOM signals. The good daytime agreement throughout the campaign period also verifies that the response of each instrument stayed stable. Contrary to the daytime results, the estimated total HOM concentration at ground level usually diverged from the tower measurement in the nocturnal boundary layer. The concentration below the canopy became even lower when temperature inversions were observed, accompanied by a decreasing ground-level O$_3$ and increasing MT concentrations. Figure 3 shows the correlation between the estimated total HOM concentrations observed at two heights. Herein, good agreement could be found for the group of points representing the concentrations around noontime ($R^2 = 0.89$). The points indicating the nighttime estimated total HOM concentrations were scattered ($R^2 = 0.28$), and the ground concentrations were found to be much lower than the tower ones.
Figure 3 Correlation between ground (x-axis) and tower (y-axis) measurements of the estimated total HOM concentrations. The black line denotes 1:1 ratio. Color code indicates the sampling time of HOMs.

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

Figure 4 Mean mass spectra with the averaging periods of daytime (09:00-15:00) and nighttime (21:00-03:00) at ground and tower levels.

4.3 Influence of nocturnal boundary layer dynamics and micrometeorological processes

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

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

Table 1 shows the overall statistics including the mean and median values of the
temperatures, O$_3$, NO$_x$, MT and estimated total HOM concentrations for the “non-
inversion night” and “inversion night” types. In the non-inversion nights, the air below
and above the canopy was relatively well-mixed. The mean and median concentrations
of the ground O$_3$ (21 ± 8 ppbv and 22 ppbv) were close to the tower values (25 ± 6 ppbv
and 24 ppbv). The slight difference might be attributed to the higher VOC emissions
(Rantala et al., 2014) and larger sink near ground level. In contrast, during the inversion
nights, the mean estimated total HOM concentration and O$_3$ at ground level were
generally much lower, only ~33% and ~69% of the tower concentrations, respectively.
Instead, the mean and median ground MT concentration (0.70 ± 0.28 ppbv and 0.70
ppbv) were ~3 times higher than the tower ones (0.24 ± 0.04 ppbv and 0.23 ppbv),
respectively. The measured NO$_x$ levels were similar in both categories and heights,
though the ambient concentrations were close to the detection limit and therefore small
differences might not be observable.

4.3.2 Case study

Two individual nights representing the “non-inversion night” and “inversion night”
types were selected and further compared. Figure 5a shows the time series of the
meteorological parameters, trace gases and HOMs measured at ground and tower
levels of one selected night of “non-inversion night” type (September 11-12, from 21:00
to 03:00). A number of measures can be used to assess the local atmospheric stability
conditions at a given layer. These measures are commonly based on either the Obukhov
length and its associated atmospheric stability parameter or a Richardson number (flux-based, gradient-based, or bulk). Because of its simplicity and the availability of high resolution mean air temperature profiles, the bulk Richardson number ($R_i$) was used here (Mahrt et al., 2001; Mammarella et al., 2007; Vickers et al., 2012; Alekseychik et al., 2013). It is calculated using:

$$
R_i = \frac{g \Delta \theta \Delta z}{\overline{\theta}(\overline{u})^2}
$$

where $g$ is the gravitational acceleration, $\Delta \bar{\theta}$ and $\Delta z$ are the mean potential temperature (10 min averaging interval, same as measurement data) and height difference between the ground and tower levels, respectively, $\bar{\theta}$ and $\overline{u}$ are the mean potential temperature and mean wind velocity at tower level, respectively. During the selected “non-inversion” night, $R_i$ was generally positive but close to 0 (shown in Figure 5a), indicating a weakly stable and relatively well-mixed (i.e. $\Delta \bar{\theta} \rightarrow 0$) condition (Mahrt, 1998; Mammarella et al., 2007). This was also confirmed using the well correlated ground and tower MT and trace gases concentrations.
Table 1 Summary of the "Non-inversion night" and "Inversion night" types.

<table>
<thead>
<tr>
<th>Type</th>
<th>Non-inversion night</th>
<th>Inversion night</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>September 6, 7, 9, 11, 15, 16, 21*</td>
<td>September 5, 8, 10, 12, 13, 14, 19**</td>
</tr>
<tr>
<td>Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tower</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean ± 1σ standard deviation</td>
<td>Temperature [°C]</td>
<td>10.2 ± 2.6</td>
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<tr>
<td></td>
<td>O₃ [ppbv]</td>
<td>25 ± 6</td>
</tr>
<tr>
<td></td>
<td>NOₓ [ppbv]</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>MT [ppbv]</td>
<td>0.31 ± 0.31</td>
</tr>
<tr>
<td></td>
<td>Estimated total HOM [10⁸ cm⁻³]</td>
<td>2.9 ± 2.5</td>
</tr>
<tr>
<td>Median</td>
<td>Temperature [°C]</td>
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</tr>
<tr>
<td></td>
<td>O₃ [ppbv]</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>NOₓ [ppbv]</td>
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</tr>
<tr>
<td></td>
<td>MT [ppbv]</td>
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<tr>
<td></td>
<td>Estimated total HOM [10⁸ cm⁻³]</td>
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</tr>
<tr>
<td>Ground</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean ± 1σ standard deviation</td>
<td>Temperature [°C]</td>
<td>10.6 ± 2.7</td>
</tr>
<tr>
<td></td>
<td>O₃ [ppbv]</td>
<td>21 ± 8</td>
</tr>
<tr>
<td></td>
<td>NOₓ [ppbv]</td>
<td>0.4 ± 0.4</td>
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<tr>
<td></td>
<td>MT [ppbv]</td>
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<td>Median</td>
<td>Temperature [°C]</td>
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<td></td>
<td>O₃ [ppbv]</td>
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<td>NOₓ [ppbv]</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>MT [ppbv]</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Estimated total HOM [10⁸ cm⁻³]</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Molecule compositions</th>
<th>Main oxidants</th>
<th>Main terminators</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO\textsubscript{monomer}</td>
<td>C\textsubscript{10}H\textsubscript{14}O\textsubscript{7}, C\textsubscript{10}H\textsubscript{14}O\textsubscript{9}</td>
<td>O\textsubscript{3}</td>
</tr>
<tr>
<td>CHON\textsubscript{monomer}</td>
<td>C\textsubscript{10}H\textsubscript{15}O\textsubscript{9}N, C\textsubscript{10}H\textsubscript{15}O\textsubscript{11}N</td>
<td>O\textsubscript{3} or NO\textsubscript{3}</td>
</tr>
<tr>
<td>CHO\textsubscript{dimer}</td>
<td>C\textsubscript{19}H\textsubscript{28}O\textsubscript{11}, C\textsubscript{20}H\textsubscript{30}O\textsubscript{14}</td>
<td>O\textsubscript{3}</td>
</tr>
<tr>
<td>CHON\textsubscript{dimer}</td>
<td>C\textsubscript{20}H\textsubscript{32}O\textsubscript{12}N\textsubscript{2}, C\textsubscript{20}H\textsubscript{33}O\textsubscript{13}N</td>
<td>NO\textsubscript{3}</td>
</tr>
</tbody>
</table>

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\textsubscript{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 O$_3$ concentration dropped by more than half (from 20 ppbv to 9 ppbv), and CO$_2$ 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 $8.6 \times 10^6$ cm$^{-3}$ to $1.7 \times 10^6$ cm$^{-3}$, and the concentration of the CHO$_{dimer}$ group decreased from $1.5 \times 10^6$ cm$^{-3}$ to ~$1.0 \times 10^5$ 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 ($1 \times 10^4$ 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 O$_3$, MT, and CO$_2$ 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 O$_3$, 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):

$$\frac{\partial \bar{c}}{\partial t} + \bar{U} \frac{\partial \bar{c}}{\partial x} + \bar{W} \frac{\partial \bar{c}}{\partial z} = -S - \frac{\partial u'c'}{\partial x} - \frac{\partial u'c'}{\partial x}$$  \hspace{1cm} (3)

$$N_1 + N_2 + N_3 = N_4 + N_5 + N_6$$  \hspace{1cm} (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 O₃ from upper layers. However, the stabilization of ground-level O₃ concentrations at non-zero values after the initial fast decrease suggests that a small amount of inflow, either via N₃ or N₅, is still taking place.

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 N₄.

Figure 6 Schematic figure showing how vertical mixing, vertical advection, and horizontal advection influence ground O₃ concentrations differently in non-inversion night and inversion night at SMEAR II station.
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, Figure7b), 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 $O_3$ 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.
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$_3^{\text{tower}}$ - 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.
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.

From micrometeorology side, 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 CO$_2$ 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. However, more direct evidence is still needed for further validation, which highlights the need for joint vertical-planar HOM studies, measuring both vertical and horizontal distribution of HOM concentrations.

5 Conclusion

Highly oxygenated molecules (HOMs) were measured above the canopy and at ground level (below the canopy) in a boreal forest environment during the IBAIRN campaign that took place in September 2016. Boundary layer dynamics and micrometeorology were found to be important factors that influence the abundance and trends of HOMs at ground level, by perturbing both their sources and sinks. In the well-mixed boundary layer (e.g. during daytime or nights without strong inversion), HOM concentrations and other measured species were overall similar between the ground and tower measurements. In contrast, much lower ground level HOM concentrations were observed when nighttime temperature inversion and formation of a decoupled layer occurred below the canopy. On one hand, the production of the ground-level HOMs could be affected by the decreasing O$_3$ concentrations and the increasing MT concentration in the shallow layer. On the other hand, the surface area to volume ratio dramatically increased in the shallow layer compared to the nocturnal boundary layer. The possibility of losses on surfaces for ground-level HOMs became much larger than
usual during inversion nights. The enhanced interaction of air in the decoupled layer with the forest floor was supported by increased concentrations of CO$_2$, emitted mainly from the ground, in this layer.

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

**Acknowledgements**

This work was supported by the IBAIRN project, the academy of Finland FCoE atmosphere, European commission Actris2 and Actris PPP, the European Research Council (Grant 638703-COALA), transnational access from ENVRI plus, and SMEAR II technical team. Q.Z. thanks ATM-DP (Doctoral Program in Atmospheric Sciences) graduate programs, John Crowley and Max Plank Institute in association with IBAIRN proposal, and the tofTools team for providing tools for mass spectrometry analysis. G.K.
acknowledges the support from the U.S. National Science Foundation (NSF-EAR-1344703, NSF-AGS-1644382), the U.S. Department of Energy (DE-SC0011461), and University of Helsinki for supporting a 3-month sabbatical leave at the Division of Atmospheric Sciences.

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