

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 in September 2016, 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. The HOM concentrations and composition distributions below and above the canopy were similar during daytime, supporting a well-mixed boundary layer approximation. However, much lower nighttime 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 clearly illustrate that near-ground HOM measurements
36 conducted under stably stratified conditions at this site might only be representative of
37 a small fraction of the entire nocturnal boundary layer. This could, in turn, influence the
38 growth of newly formed particles and SOA formation below the canopy where a large
39 majority 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 naturally charged HOM) (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 **the** boreal forest during spring. Out of the observed ambient mass spectra,
60 a 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 **autoxidation**, that is, the isomerization of
68 the RO_2 via intramolecular H-shifts and subsequent oxygen (O_2) additions; and 3)
69 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 **autoxidation were often**
77 terminated by hydroperoxyl radicals (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 ($NO_x = NO + NO_2$) to form
81 organonitrate HOM monomers ($CHON_{monomer}$). During nighttime, MT were mainly
82 oxidized by O_3 and NO_3 radicals. Furthermore, due to the lower nocturnal HO_2 and
83 NO_x concentrations, besides the production of $CHON_{monomer}$, the RO_2 products **readily**
84 **reacted** with other RO_2 to form **either** non-nitrate HOM dimers (CHO_{dimer} , mainly C_{16} -
85 20 compounds with masses between 450-600 Th after clustering with NO_3^-) or
86 organonitrate HOM dimers ($CHON_{dimer}$), depending on the oxidants **forming** the RO_2

87 radical. (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) **have been** found almost
92 uniformly distributed within the well-mixed daytime boundary layer (Chen et al., 2018).

93 In contrast, the nocturnal boundary layer was shallow with stability regimes that
94 depended on radiative cooling within the canopy and turbulent shear stresses at the

95 canopy top. In Hyytiälä, the depletion of O₃ below the canopy **has been** frequently
96 observed during nighttime, while the O₃ above the canopy was less affected (Chen et

97 al., 2018). The MT concentration at ground level increased when O₃ was depleted

98 (Eerdekens et al., 2009). The inhomogeneous distribution of the precursors and

99 oxidants below and above the canopy might further impact nocturnal HOM

100 distributions, which frames the scope of this study. Until now, all CI-API-TOF

101 deployments have been at ground level, and the main subject of inquiry here is the

102 vertical information on HOMs and the role of meteorological condition in shaping them.

103 A characterization of the HOMs at different heights provides a decisive advantage in

104 disentangling the role of non-uniform mixing within the atmospheric layers impacted

105 by strong thermal stratification, especially 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.) are presented and discussed. The influence of boundary layer dynamics on

109 the HOMs at these different heights at SMEAR II station are analyzed and characterized

110 in conjunction with auxiliary turbulence and micrometeorological measurements.

111 **3 Experimental**

112 **3.1 Measurement site description**

113 The measurements were performed at the SMEAR II station (Station for Measuring

114 Ecosystem–Atmosphere Relations) in the boreal forest in Hyytiälä, southern Finland
115 (61°51' N, 24°17' E, 181 m a.s.l., Hari and Kulmala, 2005; Hari et al., 2013) during
116 September 2016. There is no large anthropogenic emission source at or near the site.
117 The closest sources are the two sawmills ~5 km southeast of the site, and from the city
118 area of Tampere (~60 km away). The forest surrounding the station is primarily Scots
119 pine with a mean canopy height of ~17.5 m, a total leaf area index (LAI) of ~6.5 m²m⁻²
120 ², a stand density of ~1400 trees ha⁻¹, and an average diameter at breast height (DBH)
121 of ~0.16 m (Bäck et al., 2012; Launiainen et al., 2013). The forest floor is majorly
122 covered with a shallow dwarf shrub (a LAI of ~0.5 m²m⁻²) and moss layer (a LAI of ~1
123 m²m⁻²) (Kulmala et al., 2008; Launiainen et al., 2013). The planetary boundary layer
124 height at the SMEAR II station has been determined from previous studies using
125 radiosondes (Lauros et al., 2007; Ouwersloot et al., 2012) and balloon soundings
126 (Eerdeken et al., 2009). Roughly, these heights span some 400 m (March) to 1700 m
127 (August) at noontime, and 100 m (March) to <160 m (April) at midnight.

128 **3.2 Instrumentation**

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

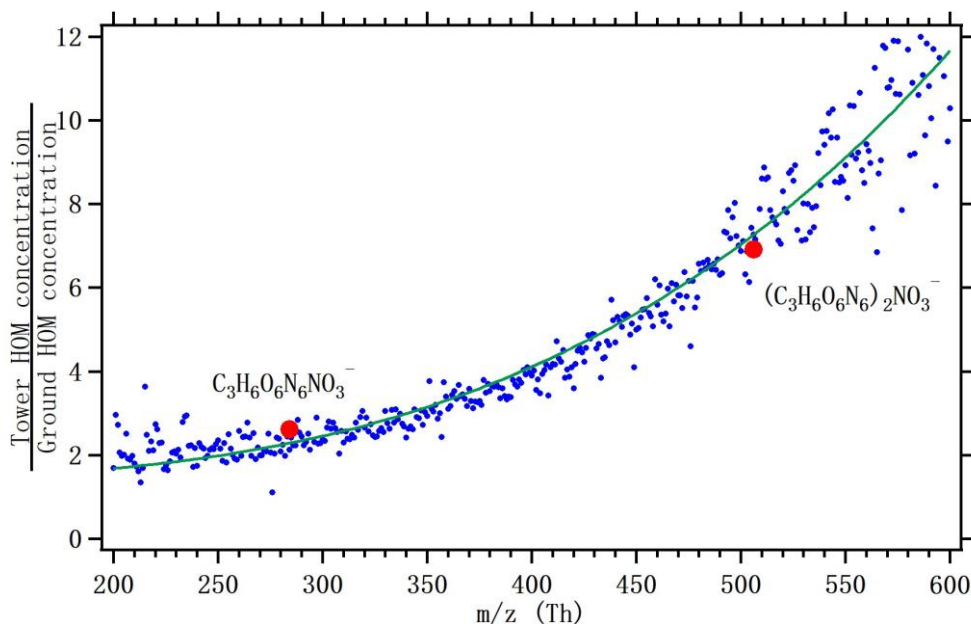
141 flow of 7 lpm (liter per minute), and then centered to an ion reaction tube surrounded
142 by sheath flow (filtered air, 35 lpm). Meanwhile, the nitrate ions carried by the sheath
143 gas, which were generated by exposing the nitric acid (HNO₃) to soft x-ray radiation,
144 were guided into the sample gas by an electrical field at ambient pressure (~100 ms
145 reaction time). Neutral molecules (M) in the sample air were ionized by either
146 clustering with charged nitrate/nitric acid ((HNO₃)_{n=0-2}·NO₃⁻) to form (M)·NO₃⁻ cluster
147 ions, or losing a proton to the charging ions to form deprotonated ions (e.g.,
148 H₂SO₄+NO₃⁻→HSO₄⁻+HNO₃). The ions then entered the APi part, which was a three-
149 stage vacuum chamber, through a pinhole. In the APi, two quadrupoles and a stack of
150 ion lenses guided the ions into the TOF mass analyzer, where ions were separated based
151 on their mass-to-charge (*m/z*) ratios. A more detailed description of this instrument has
152 been given by Junninen et al. (2010) and Jokinen et al. (2012), and discussion on
153 selectivity of this nitrate ion charging by Hyttinen et al. (2015). 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 ($\sum M$) in the numerator includes all detected ions
159 relating to compound *M*, whether deprotonated or in clusters with reagent ions, and the
160 sum of reagent ion count rates in the denominator is the total signal of the nitrate ions.
161 *C* is the calibration coefficient, which was assigned the same value for all detected
162 compounds. This assignment is only valid for compounds that cluster with the reagent
163 ions at the collision limit, such as H₂SO₄ (Viggiano et al., 1997) and have equal collision
164 rates. The collision rates of nitrate ions with H₂SO₄ and with HOMs are expected to be
165 very close (Ehn et al., 2014). Here, a calibration coefficient of 1×10^{10} molec cm⁻³,
166 estimated from previous calibrations with similar settings using sulfuric acid and
167 theoretical constraints (Ehn et al., 2014), with an uncertainty of at least -50%/+100%,
168 was used in calculating the HOM concentrations for both instruments. Ultimately, the

169 absolute HOM concentrations in this work are of secondary importance, as we focus on
170 the 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 a well-mixed boundary layer, identified with the clear and sunny weather and
178 homogeneous vertical distribution of monoterpene and other trace gases, and assumed
179 the HOM concentrations at the two heights to be the same. Thus, the relative TE was
180 obtained from the concentration ratio between the two CI-APi-TOFs at each m/z (Figure
181 1). A fitted relative TE curve ($R^2 = 0.97$), which represents how the TE of the tower CI-
182 APi-TOF was changed at each m/z over the TE of the ground one, was obtained using
183 power law regression. Weaker correlation was obtained in the 200-250 and 500-600 Th
184 mass ranges, but in the mass range where most of the HOMs were located (290-500 Th)
185 there is very little scatter around the fitted curve, clearly suggesting that observed
186 differences in the two instruments responses were mainly due to differences in TE. To
187 test our assumption of negligible vertical gradients of HOMs during daytime, we
188 analyzed the behavior of sulfuric acid. We found that the uncertainty related to this
189 assumption corresponds to a value of 26% (see Figure S1). An upper limit of uncertainty
190 relating to our TE correction (Figure 1) was also estimated, yielding a value of 10%,
191 giving a total uncertainty from these two sources of 28%. This value is much smaller
192 than the observed deviation of HOM concentrations during inversion nights, **as will be**
193 **discussed later**. Additionally, an inter-comparison between the two instruments with a
194 permeation tube containing trinitrotriazinane ($C_3H_6N_6O_6$) was conducted in the field
195 right after the campaign. The results showed good agreement with the relative TE,
196 lending confidence to the method used here. Finally, it should be noted that the

197 difference in TE between the two instruments was larger than one would normally
198 expect, since the tower CI-APi-TOF had been tuned for higher sensitivity at the largest
199 masses (at the expense of transmission at the lower masses).
200



201
202 Figure 1. The relative transmission curve between the two CI-APi-TOF mass spectrometers, determined
203 during a period of strong turbulent mixing. Inter-comparison results using a permeation tube containing
204 trinitrotriazinane ($C_3H_6N_6O_6$) are shown in red circles. The fitted green line was used to scale the
205 measured signals between the two instruments to match, in order to compare relative changes during
206 times of limited vertical mixing.

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

212
213 The MT, trace gases, and meteorological parameters were continuously monitored at
214 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)
215 on a 126 m mast ~100 m away from the location of the CI-APi-TOFs. The data at 4.2

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

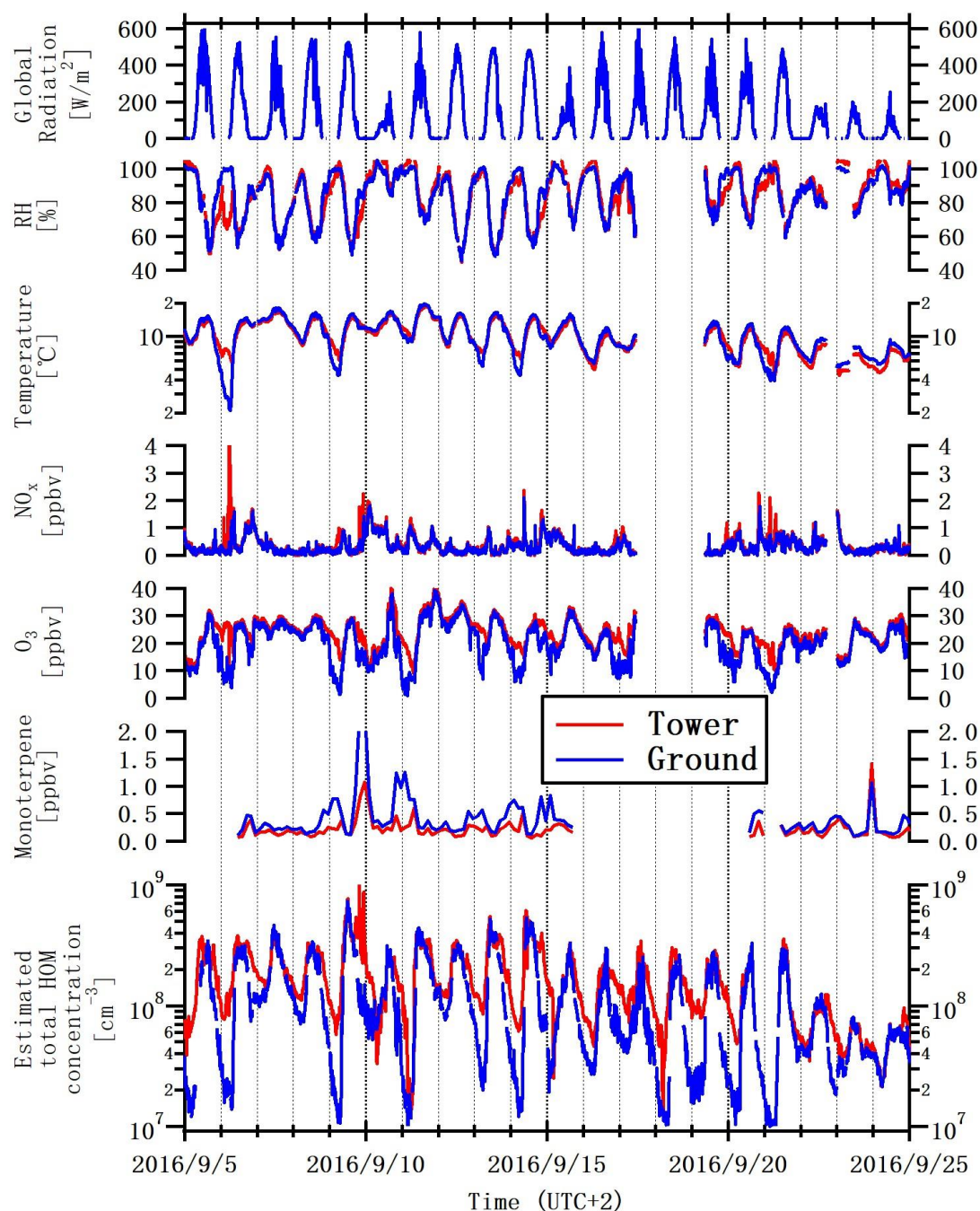
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238 **4 Results and discussion**

239 **4.1 Data overview**

240 The Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget
241 (IBAIRN) campaign was conducted from September 1 to 25, 2016. After data quality
242 checks, only the measurements collected after September 5 were used. Figure 2 shows

243 the overall time series of the meteorological parameters measured at ground and tower
244 levels, including the temperature, RH, global radiation, concentrations of trace gases,
245 MT, and total HOMs. The weather was generally sunny and clear during the campaign
246 except for a few cloudy (September 10, 15, and 22-23) and drizzling (September 24
247 and 25) days. The mean air temperature and RH observed at ground level were $10.8 \pm$
248 3.3 °C and 87 ± 13 % (1σ standard deviation), and at the tower level were 10.5 ± 3.0 °C
249 and 88 ± 14 %, respectively. The O₃ concentrations measured at ground and tower levels
250 were 21 ± 8 ppbv and 25 ± 6 ppbv, respectively. The air temperature, RH and O₃
251 measured at the two heights were close to each other during daytime. The NO_x
252 concentrations were quite low throughout the campaign, the mean NO_x concentrations
253 were mostly around the reported detection limit at 0.4 ± 0.4 ppbv (ground) and $0.4 \pm$
254 0.5 ppbv (tower), yet showed an overall good agreement between the measurements at
255 the different heights. The MT concentrations at ground level (0.38 ± 0.34 ppbv on
256 average) were generally higher than that above the canopy level (0.20 ± 0.16 ppbv).
257



258

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

261

262 The estimated total HOM concentration is representative for the overall concentration
 263 level of HOMs, and is [here](#) defined as the sum of the detected signals between ions
 264 from m/z 200 to 600 after removing identified background peaks. The gaps in the
 265 estimated total HOM [at ground level](#) were due to automatic zero-checks. During the

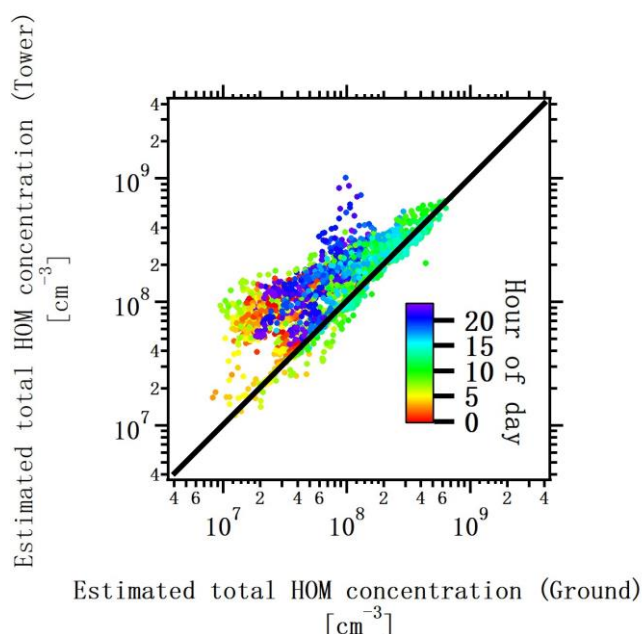
266 campaign, a significant difference was found in the estimated total HOM concentrations
267 below and above the canopy (mean and median concentrations of $1.1 \pm 1.7 \times 10^8 \text{ cm}^{-3}$
268 and $0.8 \times 10^8 \text{ cm}^{-3}$ at ground level, $1.7 \pm 1.3 \times 10^8 \text{ cm}^{-3}$ and $1.3 \times 10^8 \text{ cm}^{-3}$ at tower
269 level). The causes of these differences ($\sim 55\%$ in mean and $\sim 71\%$ in median) frame the
270 upcoming discussion.

271

272 **4.2 Inter-comparison of estimated total HOM concentrations**

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

289



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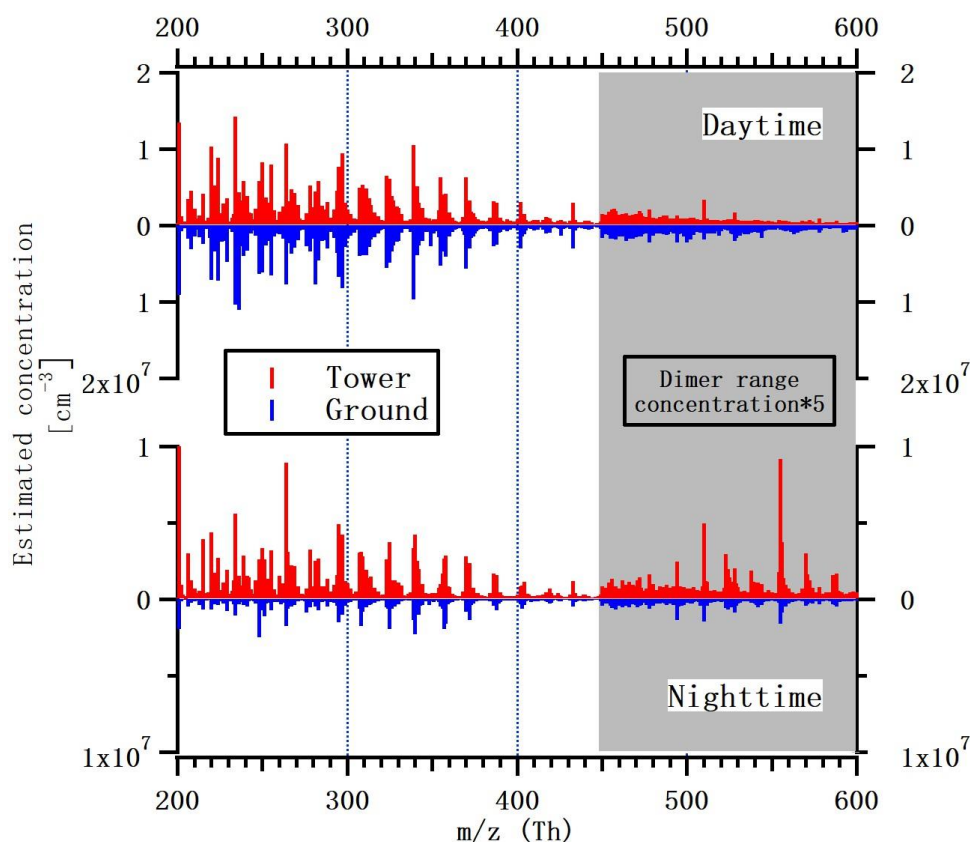
291 Figure 3. Comparison between ground (x-axis) and tower (y-axis) measurements of the estimated total
 292 HOM concentrations. The black line denotes the 1:1 ratio. Color code indicates the sampling time of
 293 HOMs.

294

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

308 during night.

309



310

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

312 (21:00-03:00) at ground and tower levels.

313 4.3 Influence of nocturnal boundary layer dynamics and micrometeorological 314 processes

315 The nighttime HOMs at ground level are likely influenced by transport processes below
316 the canopy, since the estimated total HOM concentrations were found much lower in
317 the nights when temperature inversions were observed. To further investigate the
318 potential impact of such micrometeorological phenomena on ground level HOMs, for
319 the nights during the campaign without precipitation or instrument failure, were
320 selected (14 nights in total) and categorized into 2 types based on the occurrence of
321 temperature inversions: 1) the “non-inversion night” type included 7 nights when no
322 temperature inversion was recorded; 2) the “inversion night” type category consisted

323 of 7 nights that had encountered temperature inversions, and the ground temperatures
324 were generally ~ 1 °C lower than tower temperatures during these nights.

325

326 **4.3.1 Statistics of the “non-inversion night” and “inversion night” types**

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

341

342 **4.3.2 Case study**

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

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

$$354 \quad Ri = \frac{g\Delta\bar{\theta}\Delta z}{\bar{\theta}(\bar{u})^2} \quad (2)$$

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

363

364 **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

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

366 ^{**}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-termination/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 **changed**. However, the HOM groups were still well-correlated with each other, suggesting well-mixed conditions 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.

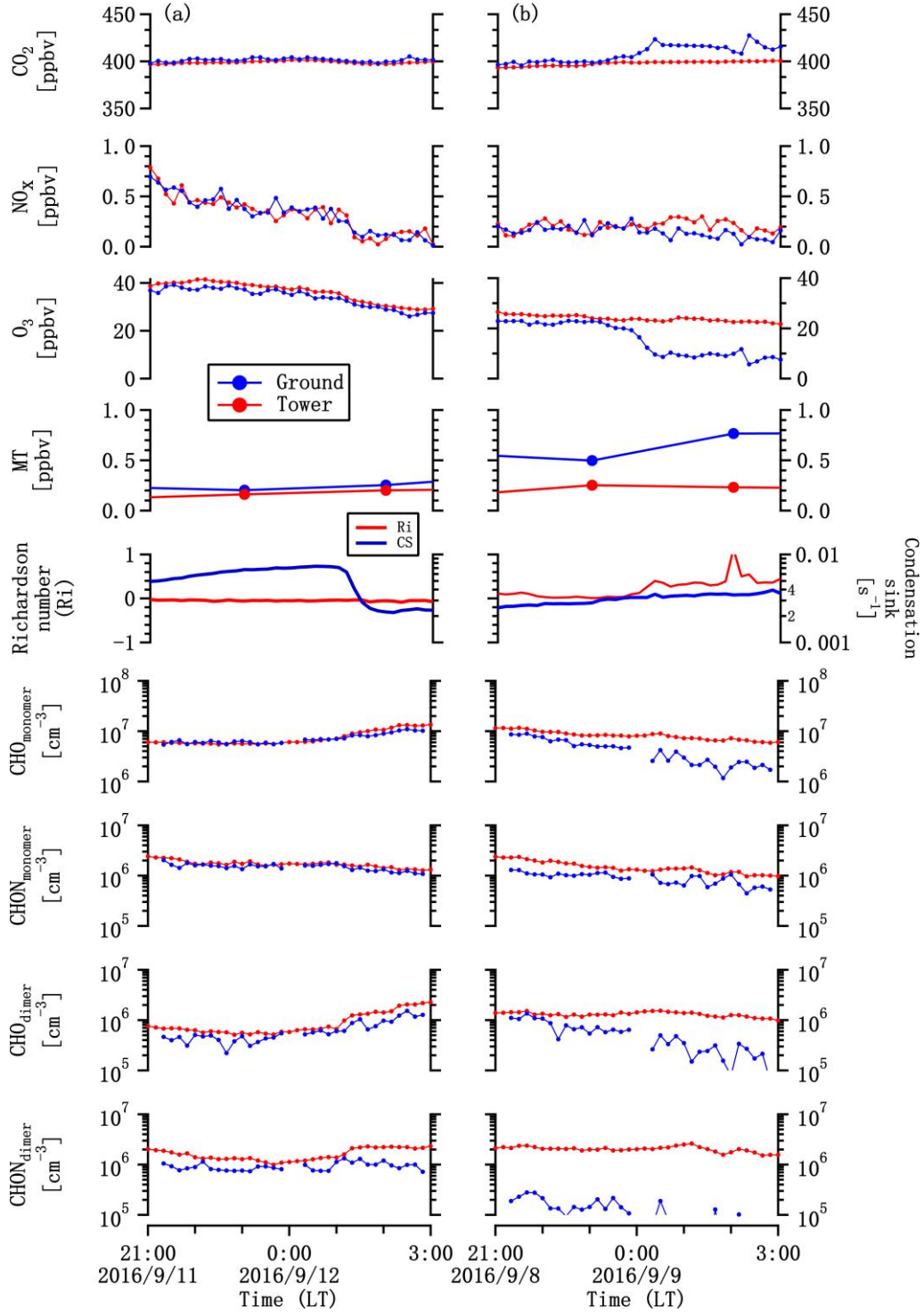


Figure 5. (a) Time series of ground and tower concentrations of CO_2 , NO_x , O_3 , MT, and selected HOM groups in the selected “non-inversion night” (September 11), and (b) “inversion night” (September 8). Ri is calculated with the meteorology data of ground and tower levels. CS is determined based 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 VOC and the 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 $\sim 0.1 \times 10^6 \text{ cm}^{-3}$. 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.

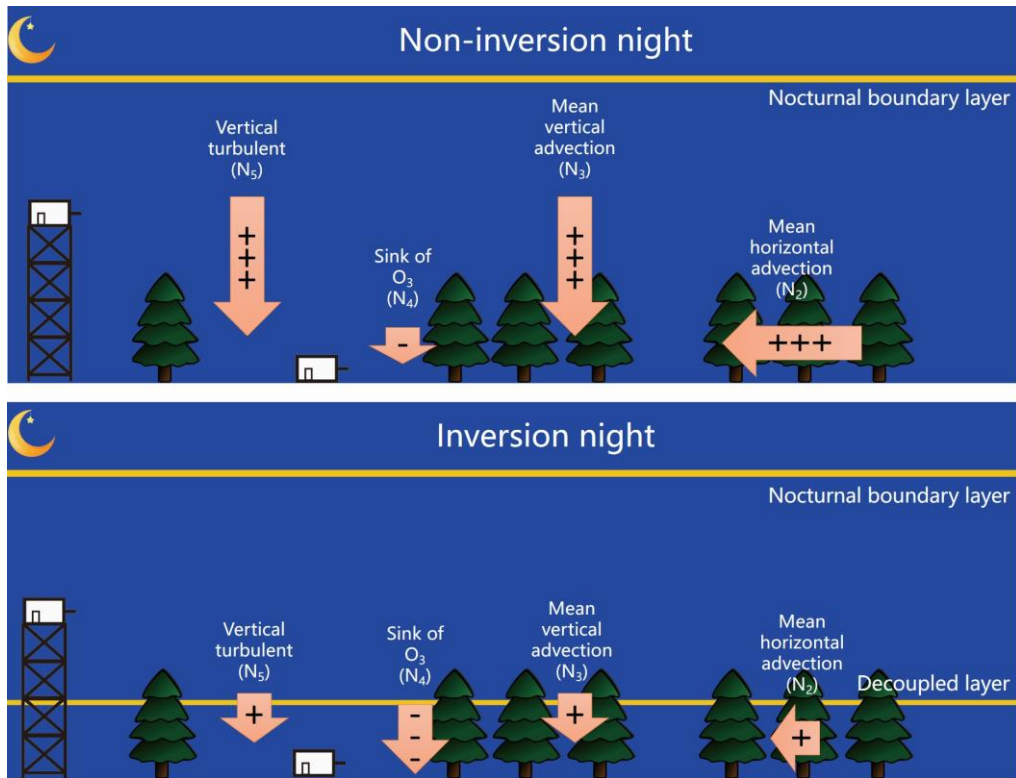


Figure 6. Schematic figure showing how vertical mixing, vertical advection, and horizontal advection influence ground level O_3 concentrations differently in non-inversion nights and inversion nights at SMEAR II station.

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 .

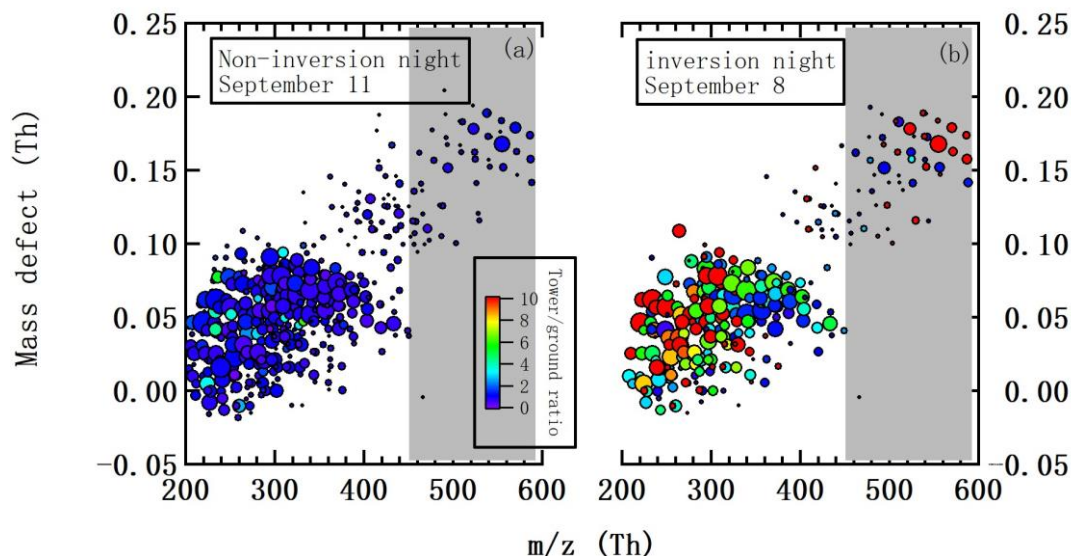


Figure 7. Mass defect (MD) plots of the selected (a) “non-inversion night” case (September 11), and (b) “inversion night” case (September 8). Color code indicates the ratios between tower/ground HOM concentrations. Grey shade area denotes the dimer range (m/z 450-600).

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), respectively. 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.

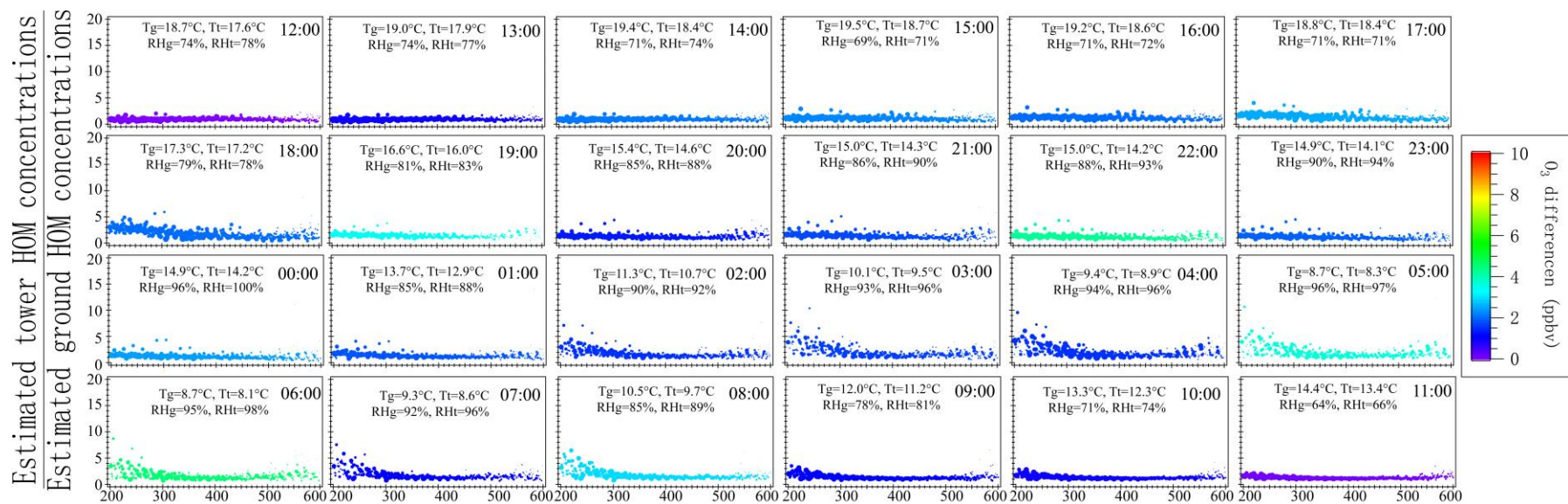


Figure 8. Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 11, 12:00 to September 12, 11:00 (non-inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3,tower} - O_{3,ground}$). Hourly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

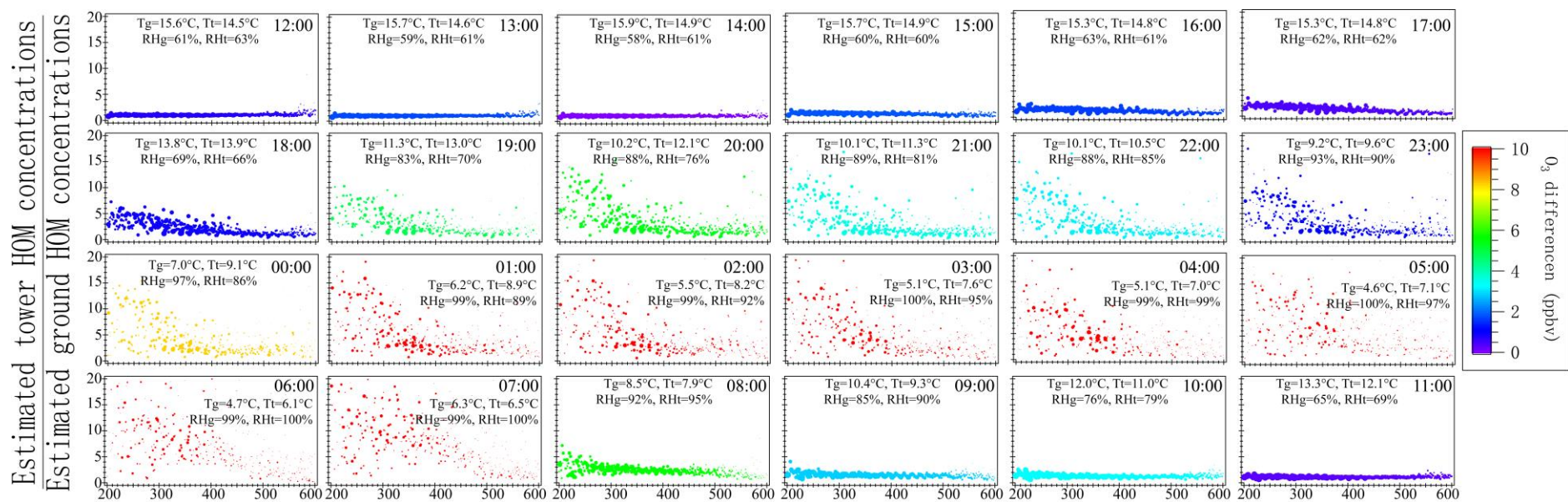


Figure 9. Hourly changes of the ratios between estimated tower and ground HOM concentrations from September 8, 12:00 to September 9, 11:00 (inversion night). Markers are sized by ground HOM concentrations and colored by O₃ difference between tower and ground ($O_{3\text{tower}} - O_{3\text{ground}}$). 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 **two** 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 **than in the tower**
331 **(shown as color scale in Figure 8 and 9)**. Absolute temperatures or RHs at the two
332 heights were not able to explain the changes. As a concrete example, good agreement
333 was observed at 07:00, September 12, while ambient temperatures were low (ground
334 and tower temperatures were 9.3 °C and 8.6 °C, respectively) and RHs were high
335 (ground and tower RHs were 92 % and 96 %, respectively), but large deviations were
336 found at 20:00, September 8, when higher temperatures (ground and tower temperatures
337 were 10.2 °C and 12.1 °C, respectively) and lower RHs (ground and tower RHs were
338 88 % and 76 %, respectively) were observed. In other words, neither low temperatures
339 nor high RHs caused large changes to our instruments. Instead, the large discrepancies
340 between the two CI-APi-TOFs were only observed when other key parameters (like
341 ozone) were found to deviate considerably between the two heights.

342

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

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

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