Review of "Vertical Characterization of Highly Oxygenated Molecules (HOMs) below and above a boreal Forest Canopy" by Zha et al.

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

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

Page 2, line 32. Suggest rewording "…attached to the forest floor."
Page 2, line 37. Suggest "This could, in turn, influence interpretation of the growth…"
Page 3, line 60. Were the HOM clusters in the laboratory experiments also "naturally charged"?
Page 3, line 79. Suggest "…compounds, with masses between…"
Page 3, line 84. Suggest "…compounds, with masses between…". In the dimerization of RO_2 radicals, what is the chemical mechanism, and what types of molecules are formed (peroxy radicals, organic peroxides, ROOR, etc.)?
Page 4, line 91. Suggest rewording. Do you mean oxidants of monoterpenes that product HOMs, or oxidants of HOMs producing other molecules or radicals?
Page 4, line 95. Is the term "sub-canopy" typical used, or would "below canopy" and/or "in canopy" be better?
Page 4, line 108. It is stated that the lower inlet is at 1.5 m, which is different than stated on page 5, line 131. Suggest making everything consistent.
Page 5, line 118-119. Suggest "…southeast of the site, and from the city area of Tampere..."
Page 5, line 124. Should "April" be "August"?
Page 5, line 128-129. Suggest "…deployed at the top…"
Page 6, line 138. Suggest rewording "…then converged to the center…"
Page 6, line 146. Suggest "..stack of ion lenses guided the ions…"
Page 6, line 153. Are you missing a summation sign before the "M" in the numerator?
Page 6, line 164-165. While it is true that absolute HOM concentrations are not as important in this work, the relative sensitivity of the two instruments is of critical importance (see earlier comment).
Page 7, line 180-181. Since the permeation tube experiments could potentially be very important, much more detail needs to be given. What is(are) the compound(s) coming from the permeation tube? What does "good" agreement mean? Can the results be included in Figure 1?
Page 7, line 184. How is the instrument tuned for maximum sensitivity at the largest masses?

Page 8, Figure 1. Is there a theoretical reason to fit the data with a power law, or did that simply provide a reasonable representation?
Page 8, lines 195 to 197. It is concerning that the various controlling parameters were not measurements at precisely the same heights as the HOM measurements. It is also concerning that these other measurements were 100 m away. Can you provide information that these differences did not affect the conclusions of this study?
Page 8, line 200. Suggest "…with a lower detection limit…"
Page 8, line 202. Suggest "…that had a lower detection limit…"
Page 8, line 205. Suggest"…lower detection limit of the NO_x analyzer was…"
Page 9, line 209. Also concerning that the aerosol measurements were not made at the same heights at the HOM measurements. What impact could this have?
Page 9, line 216. Suggest "…averaging intervals, except for the MT (in 1-hour averaging intervals)."
Page 9, line 227-229. Suggest "The mean air temperature and RH observed at ground level were…, and at the tower level were…".
Page 9, line 230-231. Suggest providing statistics for temperature, RH, and O_3 separately for daytime and nighttime.
Page 9, line 222 and page 10, line 223. This statement is confusing. The NO_x detection limit is 50 pptv (line 205), so how does this relate to mean +/- standard deviation values given. Need a bit more text to describe what was done statistically, and what the results say.
Page 20, line 235-236. Suggest "…were generally higher than those above…"
Page 11, line 242. Since the transmission efficiencies are not used in the reduction of the data, this reviewer disagrees with the statement that the sum of the signals between m/z 200 to 600 represents the total HOM concentration. This needs some reworking. If the transmission efficiencies are not know, then suggest not giving HOM concentrations, but perhaps HOM signals.
Page 11, line 246-248. Are the statistics for all the data, or just daytime or nighttime? The value after +/- is presumably the standard deviation. This needs to be stated. In the last sentence "these differences" are mentioned, but it needs to be specifically stated which differences are being referred to (e.g. differences in the means above and below (fairly small), differences in the medians (larger), etc.)?
Page 11, line 252. Suggest adding statistics to demonstrate HOM concentrations at the two heights were not different during the day.
Page 11, line 254. Suggest a figure showing that the ratio (or some other metric) of the HOM concentrations at the two heights did not change with time during the day.
Page 11, line 257. Suggest including statistics and time dependence for the two heights (as above) for nighttime data.
Page 11, line 258. Suggest showing the temperature difference between the two heights in Figure 2 to help clearly show when there are temperature inversions.
Page 11, line 261 and Figure 3. Suggest giving statistics to support the statement that there is good agreement around midday.
Page 11, line 264 and Figure 3. Suggest giving statistics for nighttime HOM concentrations to support the statement.
Page 12, line 270. Suggest "…shows the mean mass spectra…" and "…UMR, for m/z 200…" and remove "HOM measurements"
Page 12, line 283. Suggest "…strength and/or source-sink…"
Page 14, line 292. Suggest adding "likely" or "probably" in "…level are likely influenced by….".
Page 14, line 294-296. Suggest "…the potential impact of such micrometeorological phenomena on ground level HOMs, for the nights during the campaign without precipitation or instrument failure, were selected…"
Page 14, line 297. Suggest "…based on the occurrence of temperature inversions…"

Page 14, line 299. Suggest "…type category consisted of 6 nights...".
Page 14, line 301. Suggest "…lower than tower…"
Page 14, line 307. Suggest "…above the canopy was relatively…"
Page 14, line 310. Is it known that there are higher VOC emissions near the ground within forest canopies? A reference or two would be good here.
Page 14, line 315. Suggest "…similar in both categories and heights…"
Page 16, Table 1. This reviewer found the gray bars in the table (not the titles) confusing. Suggest configuring the table differently.
Page 17, line 344 and Table 2. Were these categories done for all conditions, all times (looks like it is nighttime), and both heights?
Page 17, line 363. Suggest "Roughly, Ri values in excess…" and "…stratified conditions appreciably…".
Page 17, last paragraph and Figure 5. Were these data for the ground level measurements?
Page 19, line 381. Suggest "…significant decreases after midnight."
Page 19, line 387. Suggest "…HOM concentrations might…"
Page 19, line 388. Suggest "…but also due to some other processes such as additional losses."
Page 19, line 391. Suggest giving the location of the Alekseychik et al study.
Page 19, line 392. Suggest "…Ri conditions in the…"
Page 19, line 396. Suggest "…in significantly different O_3…"
Page 19, line 397. See earlier comment about "sub-canopy".
Page 20, top paragraph. This reviewer found the use of T_1, T_2, etc confusing since capital T is usually reserved for temperature. Suggest using different symbols.
Page 20, line 418. Suggest "Note that these…"
Page 20, line 421. Suggest "area-to-volume ratio…".
Page 20, line 424. See earlier comment about "sub-canopy".
Page 22, line 452. Suggest "…however, such an analysis might only indicate the major…"
Page 22, line 453. Suggest "…holistic view of the entire mass spectrum…" or some other rewording.
Page 23, line 461. Suggest "…large differences could…"
Page 23, line 463. Suggest "…disappeared on the…"
Page 23, line 468. Suggest "…limitations still exist in this…"
Page 23, line 472. Suggest "…influence of horizontal advection could not be entirely ruled out as a contributor to..."
Page 23, line 473. Suggest "…HOM concentrations…". Suggest rewording "largely changed species"
Page 23, line 473. Suggest "…because of possible horizontal…"
Page 23, line 477. Suggest "…advection is probably minor…"
Page 23, line 479. Suggest "…evidence is still needed…"
Page 23, line 479-280. Suggest "…which highlights the need for…". Also define "joint vertical-planar HOM studies".
Page 23, line 484. Suggest "…IBAIRN campaign that took place in September 2016."
Page 24, line 486. Suggest "…that influence the abundance and trends of HOMs…"
Page 24, lines 505-507. Suggest "…close to the ground, and the effect of boundary layer…" and "…processes to HOM concentrations have…"
Page 24, line 509. Suggest "…HOM concentrations found in nocturnal inversion situations."
Page 24, line 510. Suggest "Influence of boundary…"
Page 27, line 582. There is a typo in this reference.