Responses to reviewers' comments for manuscript

Measurement report: Molecular composition and volatility of gaseous organic compounds in a boreal forest: from volatile organic compounds to highly oxygenated organic molecules

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We thank all the reviewers for their evaluation of the manuscript, and for their constructive feedback. Replies to the individual comments are directly added below in italics in green, and changes in the manuscript in italics in blue. Please note that only references that are part of the replies to the comments are listed in the bibliography at the end of this document. References in copied text excerpts from the manuscript are not included in the bibliography. Page and line numbers refer to the original manuscript text.

Reviewer #1 (responses in italics)

In their manuscript "Measurement report: Molecular composition and volatility of gaseous organic compounds in a boreal forest: from volatile organic compounds to highly oxygenated organic molecules", the authors present data from summer in a boreal forest using a suite of state-of-the-art mass spectrometers. Overall, it is scientifically valid work, and advances the important work of trying to understand the different strengths and limitations of the many new CIMS approaches. My primary concern with this work is that it is not wholly clear to me that it should be published in ACP instead of AMT. While the title pitches the science of the work, it is clear from the figures and most of the discussion that the bulk of this work is on intercomparisons between the 3 instruments(/instrument modes) and how they complement each other. While there are some plots of distributions and diurnals, etc., the focus of the discussion of these figures is again on the instrumentation. Overall, the bulk of the science here (and in my opinion, a lot of the highest value) is in the "Measurement Techniques" not the "Chemistry and Physics". In that context, I do have some technical concerns noted in my general comments below, but these are mostly addressable through changes in language and discussion and minor re-processing. I think this can and should be published with relatively minor revisions, but I'm not totally convinced that should happen in this specific journal.

We thank the reviewer for his/her overall comments on this manuscript. We understand the reviewer's concerns and we can imagine that using this suite of instruments could have led the readers to that conclusions. However, we would like to stress here, that the comparison is a fundamental part in order to understand the scientific results presented in this study. In fact, we do show some instrumental comparison results in the manuscript, but these are needed to fulfill the aim of this work, i.e., to provide a complete picture and full understanding of the molecular composition and volatility of ambient gaseous organic compounds (covering from volatile organic compounds, VOCs, to highly oxygenated organic molecules, HOMs) in a chemically rich environment. To our knowledge, this has never been achieved so far. In order to achieve this, we therefore needed to deploy and combine different measurement techniques (e.g., Vocus, MION-Br, and MION-NO₃). Without the complementary techniques, one might arrive at one-sided understandings of the "real" picture of the gaseous organic compounds in the field. In our manuscript, the complementary information obtained from Vocus, MION-Br, and MION-NO₃ provides the bulk molecular composition, oxidation extent, as well as volatility of all gaseous organic compounds (from VOCs to HOMs) in this boreal forest (see also the 2-dimentional volatility distribution in Figure R1). These results therefore provide a more comprehensive understanding of the molecular composition and volatility of atmospheric organic compounds, as well as a better basis to test and improve parameterizations for predicting organic compound evolutions in transport and climate models. We therefore believe that this study is not to introduce new "Measurement Techniques" or compare the performance of different instruments, but to target the scientific question we would like to address in the manuscript. We understand the reviewer concerns and in order to make our message clear also to future readers we have emphasized this, by adding this 2-dimentional volatility distribution figure as Figure 7a as well as the following sentences/information to the manuscript. The original Figure 7a-b are now Figure 7b-c.

Line 15 (Abstract): "In order to obtain a complete picture and full understanding of the molecular composition and volatility of ambient gaseous organic compounds (from volatile organic compounds, VOCs, to highly oxygenated organic molecules, HOMs), two different instruments were used. A Vocus [...]".

Line 85-86 (Section 1, 2nd paragraph): "[...] it still remains challenging to provide a comprehensive understanding of the molecular composition and volatility of both VOCs and OVOCs, particularly in the field. And to our knowledge this has never been achieved so far."

Line 331-332 (Section 3.4, 3^{rd} paragraph): "[...] a combined volatility distribution was plotted to obtain the bulk volatility of all measured organic compounds (with the approach described in section 2.2.1) at our measurement site (Figure 7). The combined volatility distribution covers very well from VOCs to HOMs, with varying O:C ratios and volatility ranges (Figure 7a). It therefore provides a more complete picture of the volatility distribution of gaseous organic compounds in this boreal forest. The average mass-weighted $log_{10}C_{sat}$ value representing the bulk of all measured gaseous organic compounds in this boreal forest was ~6.1 µg m⁻³. In general [...]".

Line 348-349 (Section 4, 1st paragraph): "In this paper, with an aim of obtaining a complete picture from VOCs to HOMs, the molecular composition and volatility of

gaseous organic compounds were investigated with the deployment of a Vocus and a MION API-ToF [...]".

Line 356 (Section 4, 1^{st} paragraph): "The average mass-weighted chemical composition representing the bulk of all measured gaseous organic compounds in this boreal forest was $C_{6.0}H_{8.7}O_{1.2}N_{0.1}$, indicative of the short carbon backbone and relatively low oxidation extent. Besides, [...]".

Line 362 (Section 4, 2^{nd} paragraph): "The average mass-weighted $log_{10}C_{sat}$ value representing the bulk of all measured gaseous organic compounds in this boreal forest was ~6.1 µg m⁻³. In addition, the VOC [...]".



Figure R1. Combined 2-dimentional volatility distribution for measured organic compounds parameterized with the modified Li et al. (2016) approach (Daumit et al., 2013;Isaacman-VanWertz and Aumont, 2020). Markers were sized by the logarithm of their corresponding concentrations, and marker color represents that either the compound was only measured by that instrument or the maximum concentration of the compound observed in common was detected by that instrument.

General comments:

1. There are some minor english issues - nothing egregious but quite a few cases of odd sentence structures. One of the english-as-a-first-language authors on this work should copy edit more closely.

The odd sentence structures listed by the reviewer in "Technical comments" were re-

worded according to the reviewer's suggestion.

2. In parameterizing Csat, Li et al. has a problem with nitrogen. The empirical approach was derived with very few nitrate groups, so treats nitrogen essentially as an amine. In environments where NO3 is expected to be a dominant form of organic nitrogen, this can bias the vapor pressure low by roughly two orders of magnitude per nitrogen atom. Probably not enough to change any conclusions, but with CHON representing roughly a quarter of the MION mass, it is probably enough to shift some distributions around a little. A recent paper in review in this journal describes this issue (https://acp.copernicus.org/preprints/acp-2020-1038/acp-2020-1038.pdf), and proposes a solution by treating NO3 units a OH groups, following the approach used by Daumit et al. in their parameterization.

That is a very good point and we thank the reviewer for bringing this up. We have now recalculated the VBS distributions by treating NO₃ units as OH groups following the approach by Daumit et al. (2013) and Isaacman-VanWertz and Aumont (2020). The resulting VBS distribution and compound group contribution changed a little and didn't influence our conclusions. We have updated the Figures and Table (Figure 6, 7, S10, S11, and Table 2) and the corresponding numbers in the texts. The updated VBS parameterization information was also added/rephrased in the manuscript as following:

Lines 173 (Section 2.2.2, 1^{st} paragraph): "[...] these "b" values can be found in Li et al. (2016). Due to that the empirical approach by Li et al. (2016) was derived with very few organonitrates and could therefore lead to bias for the estimated vapor pressure (Isaacman-VanWertz and Aumont, 2020), we modified the C_{sat} (298 K) of CHON compounds by replacing all NO₃ groups as OH groups (Daumit et al., 2013)."

Line 305-306 (Section 3.4, 1^{st} paragraph): "Based on the $log_{10}C_{sat}$ values of all organic compounds parameterized with the modified Li et al. (2016) approach (Daumit et al., 2013; Isaacman-VanWertz and Aumont, 2020) described in section 2.2.2, they [...]".

3. While this paper focuses most heavily on intercomparisons between the instruments, considerations of some of the pitfalls of these tools are not discussed. For example, though the potential presence of isomers is discussed in a few places, it tends to be glossed over based on relatively weak assumptions (e.g., different isomers probably have different diurnals). While a few specific spots are described below, I would just more generally caution the authors to consider that it is quite likely that the presence of

isomers is the rule, not the exception, at that different isomers may have significantly different instrument sensitivities, the authors should keep this in mind as they interpret their results. Its not really clear to me why diurnals tend to be the metrics by which isomer composition is being compared - why not point-by-point correlations, which should be high if they are truly the same isomers? One suggestion is, while isoprene is lower than monoterpenes, you may see the C5-methyltetrols (C5H12O4). This specific species is helpful because there are not a lot of likely ways to draw that formula since it is saturated and a dominant isoprene product (though there are a few peroxide options), so if multiple instruments see it, it might give some benchmark as to how correlated ions might be when they are very likely the same set of isomers.

We agree with the reviewer that different instruments may have very different sensitivities towards isomers. As also pointed out by the reviewer in the "Specific comments" 8, even with the same diurnal patterns and high point-by-point correlations, it's still possible to be different isomers (e.g., different isomers of monoterpenes could have similar diurnal patterns).

Therefore, we have abandoned the scaling approach through comparing the diurnal patterns of organic compounds observed in common by MION-Br and MION-NO3. Instead, after comparing the ambient sulphuric acid concentrations measured by *MION-Br* and *MION-NO*³ (See Figure R2a), we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO₃. The reason why we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO₃ is because Br mode has been found to be more sensitive to RH (Hyttinen et al., 2018) and the high RH in the calibration kit (Kürten et al., 2012) could cause some uncertainties in its calibration factor. This scaling approach is more reasonable since the calibrations were done for sulphuric acid (compound representing the kinetic limit sensitivity; Viggiano et al., 1997; Berresheim et al., 2000) for MION-Br and MION-NO₃. The scaling factor of sulphuric acid was determined to be 0.53 (median value; see Figure R2b). We have therefore deleted the sentence in Line 133-137 and added the following sentence in Line 130 (Section 2.2.1, 1st paragraph) of the manuscript: "By comparing the ambient H_2SO_4 concentrations measured by MION-Br and MION-NO₃, the median value (0.53) was used to scale down the H_2SO_4 concentration measured by MION-Br, due to that the high RH in the calibration kit could cause some uncertainties in its calibration factor (Hyttinen et al., 2018; Kürten et al., 2012)." The corrected organic

concentrations for MION-Br were also updated in Figure 1, 2, 7, S5, S10, and S11.

Besides, based on the reviewer 1's and reviewer 2's suggestion we have also calculated the correlation coefficients for several dominant CHO and CHON species (including $C_7H_{10}O_4$, $C_8H_{12}O_4$, $C_{10}H_{15}NO_{6-7}$) discussed in the manuscript, for a simplified examination of isomer content for individual compound (see Table R1). The corresponding information was added to Line 293 (Section 3.3, 2nd paragraph) of the manuscript: "[...] The inconsistent trends in time series and the varying correlations of these above-mentioned dominant CHO and CHON species indicate different isomer contributions detected by different measurement techniques (Figure S8 and Table S3). Similar behaviors were also evident for [...]". The original Figure S7-S9 are now Figure S9-S11.



Figure R2. Sulphuric acid concentrations measured by MION-Br and MION-NO₃ (circles in yellow). (*a*) before scaling for MION-Br data (circles in blue); (*b*) after scaling for MION-Br data (circles in green).

Table R1. Pearson's R correlations for dominant CHO and CHON species amongdifferent measurement techniques.

Compound	Vocus vs. MION-Br	Vocus vs. MION-NO ₃	MION-Br vs. MION-NO ₃
$C_7 H_{10} O_4$	0.63	0.65	0.96
$C_8H_{12}O_4$	0.64	0.66	0.96
$C_{10}H_{15}NO_{6}$	0.35	0.36	0.93
$C_{10}H_{15}NO_{7}$	0.47	0.43	0.94

4. Similarly, the role of fragmentation in these results is not considered deeply, though PTR is known to fragment. What does this mean for measured mass? For instrument overlap? For average elemental composition? Is this related to the flat diurnal in Vocus

CHO and CHON? These instruments are amazing advances, but they do have limitations in their interpretation, and these limitations are not always deeply considered in this work.

We agree with the reviewer that PTR causes non-negligible fragmentation. However, we do not find it plausible the flat diurnal patterns of total CHO and total CHON compounds are caused by fragmentation. As shown in Figure 5, these individual CHO or CHON compounds measured by Vocus do have diurnal variations between day and night. Compared to MION-Br and MION-NO3, Vocus detects both much less oxygenated compounds and comparatively more oxygenated compounds. For CHO compounds, the much less oxygenated CHO compounds mostly peak at night, while the comparatively more oxygenated CHO compounds peak during daytime (Li et al., 2020). *Therefore, when they are summed up, the total CHO compounds may have a relatively* flat diurnal pattern. For CHON compounds, the much less oxygenated CHON compounds mostly present high concentrations at night, with morning and evening peaks; the comparatively more oxygenated CHON compounds present higher concentrations during daytime (Li et al., 2020). Therefore, their summed-up concentration may also show a flat diurnal pattern. As we state at several occasions in the manuscript (e.g., Line 69-72, Line 241-243), the fragmentation may partly explain why Vocus is not preferred for detecting dimers. With the fragmentation present for Vocus, it may influence our understanding of the elemental composition, absolute signal, and volatility to some extent. The carbon backbone and signals measured by *Vocus may be biased to be shorter and lower, while the volatility may be biased to be* higher. However, in order to fully understand the fragmentation pattern, it would require comprehensive laboratory experiments to study on this, which however lies outside the scope of this paper. To clarify more on the role of fragmentation and the potential reasons for the flat diurnals in Figure 4, the following information was added to the manuscript:

Line 154 (Section 2.2.1, 2nd paragraph): "Signals were pre-averaged over 30 min before the analysis. We stress here that the fragmentation of organic compounds inside the instrument (Heinritzi et al., 2016) may bias the signals of parent ions towards lower values and the signals of fragment ions towards higher values."

Line 179 (Section 2.2.2, 3^{rd} paragraph): "Besides, the fragmentation of organic compounds inside the instruments (e.g., Vocus) may also bias the C_{sat} results towards

higher volatilities (Heinritzi et al., 2016)."

Line 231 (Section 3.2, 1st paragraph): "[...] respectively. We stress here that the fragmentation of organic compounds inside the Vocus may bias the chemical composition towards shorter carbon backbone."

Line 278-279 (Section 3.3, 1st paragraph): "[...] CHO compounds measured by Vocus [...] have also been reported to follow more the CH trends (Li et al., 2020b). Their relatively flat diurnal pattern could be resulted from the smearing effect after summing up the much less oxygenated CHO molecules (mostly peak at night) and comparatively more oxygenated CHO molecules (mostly peak during daytime) (Li et al., 2020b). "

Line 284-286 (Section 3.3, 1st paragraph): "The potential reason could be partly due to its lower sensitivity towards larger organonitrates (see Fig. S5) caused by their losses in the sampling lines and on the walls of the inlet (Riva et al., 2019) and/or their fragmentation inside the instrument (Heinritzi et al., 2016). Another potential reason could be resulted from the smearing effect after summing up the much less oxygenated CHON molecules (mostly peak at night or early morning) and comparatively more oxygenated CHON molecules (mostly peak during daytime) (Li et al., 2020b)."

Line 316 (Section 3.4, 1^{st} paragraph): "We stress here that the fragmentation of organic compounds inside the Vocus may bias the C_{sat} results towards higher volatilities."

Specific comments:

1. "VOC" is usually pluralized as VOCs when used in a plural sense.

Changed as suggested throughout the manuscript.

2. Line 70-71. This sentence isn't quite grammatically correct, re-word.

Sentence rephrased as following: "However, Vocus PTR-ToF is not preferred for detecting HOMs or dimers (Li et al., 2020b; Riva et al., 2019). The potential reason for the latter case could be resulted from the fragmentation inside the instrument (Heinritzi et al., 2016) and/or losses in the sampling lines and on the walls of the inlet (Riva et al., 2019)."

3. Line 73-76. Run-on sentence, somewhat confusing.

Sentence rephrased as following: "The detection of less oxygenated VOCs (including less oxygenated dimers) and more oxygenated VOCs (including HOMs) can be well achieved by another instrument: an Atmospheric Pressure Interface Time-of-Flight mass spectrometer (API-ToF) coupled to a novel chemical ionization inlet, Multi-scheme chemical IONization inlet (MION; Rissanen et al., 2019). Via the fast switching between multiple reagent ion schemes (i.e., bromide and nitrate), it has been found that [...]".

4. Line 74. Why isn't Interface capitalized in APi-ToF?

Changed to "API-ToF" throughout the manuscript.

5. Line 75. It's not clear to me: is MION just a switching reagent ionization approach, which has been shown previously using a PTR, but as applied to an API-ToF? Because it is discussed in the same "breath" as the the Vocus, my initial reading is that it is a functionality of the Vocus, but I gather that the MION instrument is a physically distinct ToF-CIMS. This confusion makes it a bit hard to understand or parse the rest of this paragraph. I think this paragraph just needs some editing and further clarification and detail.

Similar to MION inlet, Vocus is also possible to run multi-ion operation (Breitenlechner et al., 2017;Krechmer et al., 2018). However, the MION inlet is different from Vocus inlet. As we state in Line 110-114 (Section 2.2.1, 1st paragraph) of the manuscript, MION is a novel chemical ionization inlet, which can switch among nitrate, bromide, and API mode. After coupling to an API-ToF, atmospheric neutral OVOC molecules (both less oxygenated VOCs and more oxygenated VOCs including HOMs) and naturally charged ions can be detected. More description of MION API-ToF can be found in Rissanen et al. (2019). For clarification, we have added/rephrased the sentences in the manuscript as following:

Line 15 (Abstract): "In order to obtain a complete picture and full understanding of the molecular composition and volatility of ambient gaseous organic compounds (from volatile organic compounds, VOCs, to highly oxygenated organic molecules, HOMs), two different instruments were used. A Vocus [...]".

Line 73-76 (Section 1, 2nd paragraph): "[...] can be well achieved by another instrument: an Atmospheric Pressure Interface Time-of-Flight mass spectrometer (API-

ToF) coupled to a novel chemical ionization inlet, Multi-scheme chemical IONization inlet (MION; Rissanen et al., 2019). Via the fast switching between multiple reagent ion schemes (i.e., bromide and nitrate), it has been found that [...]".

6. Line 108. "Finnish winter time" is confusing, since it is in spring. Perhaps "Finnish Winter Time" or "Eastern European Time (EET)" which I think is the general term for UTC+2 in Europe.

Changed to "Eastern European Time".

7. Line 126-129. Is the assumption the sulphuric acid represents the kinetic limit sensitivity, so is used as a floor for org? If so, that should be explicitly mentioned, otherwise it's not clear why the org sensitivity factors are being determined by sulphuric acid.

The reviewer is right. Sulphuric acid has been reported to represent the kinetic limit sensitivity (Viggiano et al., 1997;Berresheim et al., 2000) and therefore has been used as a floor for organic compounds (e.g., Ehn et al., 2014;Berndt et al., 2015). With the maximum sensitivity applied, the organic compound concentrations therefore represent a lower limit. The corresponding information was add to Line 128-130 (Section 2.2.1, 1^{st} paragraph) of the manuscript: "[...] the calibration factors, C_{Br} - and C_{NO_3} , for sulphuric acid (H₂SO₄, compound representing the kinetic limit sensitivity; Viggiano et al., 1997; Berresheim et al., 2000), were determined to be [...] With the maximum sensitivity applied, the concentrations therefore represent a lower limit. The uncertainties in [...]".

8. Line 134-137. Similar diurnal patterns is a poor approach to determining isomer content. Take, for example, monoterpenes, for which there are usually around a dozen isomers, but all are expected to have a similar diurnal. Point-to-point correlations (R2) might be a better metric than diurnals, but it will still suffer from this example issue (just perhaps less so). Since you are comparing across two different ionizations, this approach is perhaps a bit more reasonable (if an ionization scheme sees one group of isomers, the other one probably does too), but it is still has serious issues. Isomers can vary in their sensitivity by an order of magnitude within an ionization scheme (e.g., iodide, Lee et al. CITE), so one ionization scheme could see one set of isomers with high sensitivity, and the other could see a different set with high sensitivity, but these

could still have similar diurnals. All-in-all, I'm sympathetic to the need to do something about potential overlap and the uncertainties in bulk calibration of CIMS, but scaling one instrument to another based on diurnals is built on fairly shaky assumptions that need a more robust examination. Are there trends in correlations between ionizations as a funciton of ion elemental ratios that might allow you to tease out when they are seeing the same isomers and when they are not? Or any other features within the data? Simply put, similar diurnals is insufficient evidence for "likely to be the same species", and more caution is warranted in acting on this conclusion.

Here we refer to our response to the "General comments" 3. We agree with the reviewer that sensitivity can vary between different ionization methods, even for different isomers. We have therefore abandoned the scaling approach through comparing the diurnals of organic compounds observed in common with MION-Br and MION-NO3. Instead, after comparing the ambient sulphuric acid concentrations, we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO3. This scaling approach is more reasonable since the calibrations were done for sulphuric acid (compound representing the kinetic limit sensitivity; Viggiano et al., 1997;Berresheim et al., 2000) for MION-Br and MION-NO3. Besides, we have also added the correlations for several dominant CHO and CHON species (including $C_7H_{10}O_4$, $C_8H_{12}O_4$, $C_{10}H_{15}NO_{6-7}$) discussed in the manuscript in Table S3 for a simplified examination of isomer content for individual compound (see also Table R1).

9. Line 155-157. This is a better/more conservative approach to handling overlap.

We agree on this. Different measurement techniques may have different sensitivities towards the same molecular formula. Therefore, this approach is preferred when combining different measurement techniques (Stolzenburg et al., 2018).

10. Line 182. A Pt100 should be defined/described.

The information for Pt100 was added to the manuscript as following: "[...] with a Pt100 sensor (Platinum resistance thermometer with a resistance of 100 ohms (Ω) at 0 °C) inside [...]".

11. Line 205. Is this the full list of compounds excluded, or just an example list? Is the full list provided somewhere? Would it be helpful to also add that data, for instance as Vocus_LL or some other signifier? That would be interested from an organic carbon

budget perspective.

The compounds excluded from Vocus data in the manuscript are an example list. The full list were added as Table S1. The original Table S1 is now Table S2. Organic compound concentrations including these relatively long-lived species were added to Figure S4. The corresponding information was added to Line 205-206 (Section 3.1, 1st paragraph) of the manuscript: "Note that relatively long-lived compounds like ethanol, acetone, and acetic acid, are excluded from Vocus data presented in this study in order to focus on compounds actively involved in the fast photochemistry (all excluded compounds are listed in Table S1 and the time series of total organic compound concentrations including them are shown in Figure S4)."

12. Line 233. Is this average composition of organic gases, or does it include ACSM measured organic particles?

The average molecular composition is only for gaseous organic compounds, and therefore doesn't include ACSM organic particles. The information was added to Line 232 (Section 3.2, 1^{st} paragraph) of the manuscript: "And the average mass-weighted chemical composition representing the bulk of all measured gaseous organic compounds [...]".

13. Line 238. "followed-by groups" is not something I've seen before in written English.

We changed it to "The second most abundant group".

14. Lines 226-243. While PTR is fairly soft, it is known to have non-negligible fragmentation (Yuan et al., 2017, e.g., Figure 5 therein). How might this impact both the quantification of the total measurement by this instrument, and/or understanding of the elemental compositions? This issue of course does not involaidate the Vocus, or these measurements, but the effects of fragmentation and its impacts on the potential interpretation and conclusions in this work should be considered and discussed.

We have added more discussions about the effect of fragmentation inside Vocus on our results and interpretation including the quantification, the elemental composition, and the volatility. Please see our response for the "General comments" 4.

15. Line 268. It's not clear to me the C20 is necessarily diterpenes. While the SI does show some diterpenes (which is very exciting and interesting, and sadly buried in the

SI), monoterpenes are known to dimerize and for C20 compounds. I note that the bar on C20 looks like it is mostly O>=12, so highly oxygenated. Is this not just monoterpene dimers? It might provide some insight into the influence of monoterpene-dimers vs. diterpene-monomers to looks at distributions of oxygen number.

The $C_{20}HO(N)$ compounds can be diterpene monomers or monoterpene dimers, depending on the oxidation extent. The C_{20} bar in the bottom panel of Figure 3 is not obvious due to the small contributions of C_{20} compounds. C_{20} compounds with the number of oxygen atoms bigger than 12 were found to contribute only ~41% to the total C_{20} compounds measured by MION-NO3. Besides, from the distribution of CHO and CHON compounds as a function of number of oxygen atoms vs. number of carbon atoms (Figure S5), we also clearly see substantial contributions of less oxygenated C_{20} compounds, which are likely to be diterpene monomers. To clarify this, the following sentence was added to Line 269 (Section 3.2, 3^{rd} paragraph) of the manuscript: "[...] We emphasize here that using the number of carbon atoms as a basis to relate the CHOX to their precursor VOCs is a simplified assumption, as negative or positive artifacts can arise from fragmentation or accretion reactions (Lee et al., 2016)."

16. Line 284-286. Why would this smearing occur for Vocus data, but not the other data? Is it related to the tendency for nitrates to fragment in PTR?

The fragmentation for nitrates could be part of the reason. But the smearing effect could also happen after summing up the much less oxygenated CHON molecules (mostly peak at night or early morning) and comparatively more oxygenated CHON molecules (mostly peak during daytime) (Li et al., 2020b). Please see our response for "General comments" 4 for more details on the potential reason for the flat diurnal patterns.

17. Figure 1. Why use ppb for inorganics and cm-3 for organics? Organic gases are more commonly reported as ppb.

Both units are commonly used to report the concentrations of organics (e.g., Bianchi et al., 2019; Stolzenburg et al., 2018;Li et al., 2020). Different from the relatively more abundant levels of inorganics (e.g., ppbv), the abundance of many organic compounds are in trace levels and can vary across several orders of magnitude (see Figure 7). For example, the individual HOM concentration can vary between 10⁴ to 10⁸ cm⁻³ (roughly 10⁻³ to 10 pptv). Nevertheless, for better consistency with other Vocus publications we have converted the unit of the concentrations in Figure 1, 7, S4, and S11 to pptv or

ppbv.

18. Figures 6 and 7. I recognize why the authors chose to plot these distributions on a log scale, but a bar chart on a log scale is inherently inaccurate/confusing, especially a stacked bar chart. Because there is no "zero", drawing a line to zero on a bar chart creates a wholly arbitrary scaling, which means the bar size is no longer in any way proportional to quantity. Consider Figure 7 at log(Csat)=7. While roughly 99.9% of the concentrationis measured by the Vocus, more than half the bar is blue. At the same time, if the bars were stacked in the opposite order, MION-Br would be negligibly small sitting on top of the Vocus. Similarly, the scale on the x-axis could reasonably be altered to start at 10[°]3 or 10[°]2 instead of 10[°]4, and that choice would dramatically change the areas of only the bottom bar in the stack. What the solution here is, I'm not sure, but I strongly recommend the authors make some other style choice.

Is it worth splitting these figures across two figures? It seems to me that 6a and 7a are showing basically the same data - couldn't you should had 6b-d to Figure 7. Relatedly, though they seem to be plotting the same data, I can't reconcile them quantitatively. Again, as an example $\log(\text{Csat})=7$. In Figure 6a, this looks like roughly: Vocus 15%, Br 8%, NO3 3%. In Figure 7a, the ratio is Vocus: stack from $10^{7.5}$ to $10^{10} = 10^{10}$, Br: stack to $10^{7.5}$, NO3:negligible. That is a ratio of Vocus:Br = 300:1 instead of 2:1. I wonder of this issue is related to the stacked log plot issue described above.

We understand the reviewer's concerns. The use of stacked bar chart in log scale is, however, not an exception in our manuscript. Stolzenburg et al. (2018) also used this kind of plot when combining different measurement techniques, since the concentrations measured by different instruments can vary across several orders of magnitude. Although the bar height is not proportional to the quantity due to the log scale, the y axis indicates the quantity of each bar, and the contributions of each volatility class were also summarized in Figure 6b-d and Table 2. With a linear scale, however, the information e.g. from MION-NO₃ would be totally buried to "zero" although it's not the case at all. Therefore, we prefer to keep the stacked bar chart in Figure 6a and 7a in their current version in the manuscript.

As for the Figure 6a and Figure 7a, they actually do not show the same data. Figure 6a shows the individual volatility distribution measured by each measurement techniques without taking into account the absolute quantity, since the goal is to show

the distinct volatility distribution of different measurement techniques. However, the goal of Figure 7a is to obtain the complete picture of the volatility distribution as well as the bulk volatility of all measured organic compounds (from VOCs to HOMs) at our measurement site (see also Figure R1). Therefore it shows the absolute concentrations of all measured organic compounds after the combination of the three ionization techniques (i.e., Vocus, MION-Br, and MION-NO₃) as we mentioned in Line 155-157 (section 2.2.1, 3rd paragraph) of the manuscript (i.e., "[...] for organic compounds observed in all ionization techniques the highest concentration was used."). With the absolute concentrations of all measured organic compounds in Figure 7a, it also provides a better basis to test and improve parameterizations for predicting organic compound evolutions in transport and climate models. With the volatility distribution figure (Figure R1) as Figure 7a as well as more information to the manuscript as following. The original Figure 7a-b are now Figure 7b-c.

Line 331-332 (Section 3.4, 3rd paragraph): "[...] a combined volatility distribution was plotted to obtain the bulk volatility of all measured organic compounds (with the approach described in section 2.2.1) at our measurement site (Figure 7). The combined volatility distribution covers very well from VOCs to HOMs, with varying O:C ratios and volatility ranges (Figure 7a). It therefore provides a more complete picture of the volatility distribution of gaseous organic compounds in this boreal forest."

Line 701 (Figure 7 caption): "Figure 7. (a) Combined 2-dimentional volatility distribution for measured organic compounds parameterized with the modified Li et al. (2016) approach (Daumit et al., 2013;Isaacman-VanWertz and Aumont, 2020). Markers were sized by the logarithm of their corresponding concentrations, and marker color represents that either the compound was only measured by that instrument or the maximum concentration of the compound observed in common was detected by that instrument; (b) Stacked bar plot of combined volatility distribution; (c) resulting pie chart for the contributions of VOC, IVOC, SVOC, LVOC, ELVOC, and ULVOC."

Reviewer #2 (responses in italics)

Huang and coauthors compared the measurements of gas-phase organic compounds by Vocus PTR-ToF, Nitrate CIMS and a Br CIMS. They found different chemical compositions from the three different techniques. The measured diurnal profiles from the three techniques are different even for compounds with the same molecular. The authors claimed that a more comprehensive understanding of molecular composition and volatility can be obtained by this kind of comparison and combined analysis. This manuscript is generally well written. I can be accepted in Atmospheric Chemistry and Physics, after addressing my following comments.

1. Line 115, a stainless-steel tube of 0.9 m long inlet was used for the MION API-TOF. Will SVOC and HOMs loss to the stainless-steel tube. Why not using PFA, See Deming et al., 2019 AMT.

One reason for using stainless-steel tube for MION API-ToF is to avoid strong fluorinecontaining contaminations in the measured gaseous organic compounds from PFA tubing. However, the main reason is to avoid the electrostatic removal of atmospheric ions by plastic tube (electrostatic charges present on plastic walls) during the API mode measurement of MION API-ToF. Besides, the inlet diameter (1 inch (25.4 mm) OD) is much larger than a normal gas-phase PFA tube (typically 6mm OD), and the inlet flow rate (20 L min⁻¹) is also large with only a minor fraction going into the instrument. Broadly, our sampling strategy for low-volatility organic gases is the same as for highly reactive radicals. We assume that they are likely lost on every collision with inlet walls, and so design the inlet and inlet flows to minimize wall contact. It is therefore reasonable to assume the SVOC and HOM losses would not be high. The information was added to Line 115-116 (Section 2.2.1, 1st paragraph) of the manuscript: "Gaseous organic compounds were sampled via a stainless steel tube (1 inch outer diameter) of ca. 0.9 m length and a flow rate of 20 L min⁻¹. Due to the large inlet diameter and flow rate, the SVOC and HOM losses are expected to be insignificant."

2. Line 120: I am not sure about how data processing was done for Br CIMS. As Bromine has two isotopes, 79 and 81. Then, each compound would generate at least two product ions, even there is no fragmentation or other chemical pathways. Did the author take into account both, or just one? Will this cause problem to detect compounds with two hydrogen apart (e.g. CxHyOz and CxHy+2Oz)?

The reviewer is right. The data analysis for MION-Br is more complicated due to the two stable isotopes of bromide, which share similar relative isotopic abundance of bromide. The data analysis packages, "toftools" (developed by Junninen et al. (2010)), which was used for the MION-Br data analysis, would automatically fit the corresponding ⁸¹Br⁻ clustered compounds when we fit the ⁷⁹Br⁻ clustered compounds (also true for e.g. ¹³C and ³⁴S when we fit ¹²C-containing or ³²S-containing compounds). Therefore we didn't manually add the ⁸¹Br⁻ clustered compounds into the peaklist during the high resolution fitting, but their presence has been taken into account for all the peaks. Besides, the calibration factor C_{Br} - for sulphuric acid was also determined in a similar way.

As for the detection of compounds with two hydrogens apart, it is not a big problem for us due to the long ToF (LToF) used (with a mass resolving power of ~9000) and also to the positive mass defect effect of hydrogens (2.0156 (1.0078*2) for 2 hydrogens). Therefore, $C_xH_yO_z$ clustered with ⁸¹Br⁻ could be separated from $C_xH_{y+2}O_z$ clustered with ⁷⁹Br⁻.

For clarification, we have added the corresponding information to the manuscript as following:

Line 110 (Section 2.2.1, 1st paragraph): "An API-ToF (Tofwerk Ltd.; equipped with a long ToF with a mass resolving power of ~9000) coupled to a recently developed multi-scheme chemical ionization inlet (MION [...]".

Line 127 (Section 2.2.1, 1^{st} paragraph): "[...] The two stable isotopes of bromide (⁷⁹Br⁻ and ⁸¹Br⁻) share similar relative isotopic abundance, but only the compound clustered with ⁷⁹Br⁻ was used for the quantification (Sanchez et al., 2016), as the calibration factor, C_{Br^-} , was also calculated in a similar way. Following the approach by [...]".

3. Line 120-125: As Br CIMS is kind of new reagent ion, can the authors provide some information about the types of compounds can be measured by Br CIMS. It would be if the advantages and also disadvantages for Br CIMS can be provided somewhere in the manuscript.

The Br-CIMS has been found to be capable of detecting hydroperoxyl radicals (Sanchez

et al., 2016), peroxy radicals formed by autoxidation, and less-oxygenated organic molecules (Rissanen et al., 2019). Based on a computational study by Hyttinen et al. (2018), the instrumental sensitivity of Br^- as the reagent ion is similar or even higher than that of iodide (Γ^-) towards OVOCs depending on humidity. We have also stated this at few occasions of the manuscript (e.g., Line 72-76, Line 116-117) that the detection of less oxygenated VOCs (including less oxygenated dimers) can be achieved by MION-Br. And the results in Figure 2a (i.e., the mass defect plot), Figure 3 (i.e., the contribution of CHOX compounds with different number of oxygen atoms as a function of number of carbon atoms), and Figure S5 (i.e., the distribution of CHO and CHON compounds as a function of number of oxygen atoms vs. number of carbon atoms) support this statement. For better elaboration, more information about the capability of MION-Br was added to the manuscript as following:

Line 78 (Section 1, 2nd paragraph): "Br-CIMS has been found to have similar or even higher sensitivities than that of iodide-CIMS towards OVOCs depending on humidity (Hyttinen et al., 2018). It has also been used for the detection of hydroperoxyl radicals (Sanchez et al., 2016) and peroxy radicals formed by autoxidation (Rissanen et al., 2019). In addition to [...]".

Line 116-117 (Section 2.2.1, 1^{st} paragraph): "Through the fast switching between the two reagent ion schemes, Br^- and NO_3^- , less oxygenated VOCs (including less oxygenated dimers) and more oxygenated VOCs (including HOMs) can be measured, respectively (Rissanen et al., 2019)."

4. Line 136: why to scale the measurement of Br CIMS, how 0.3 is obtained. Are you claiming the sensitivity variations are same between NO3- and Br-. As many of the conclusions rely on good quantification for all of the instruments, a better of quantification of Br CIMS should be conducted.

We agree with the reviewer that different instruments may have very different sensitivities towards isomers. Please refer to our response to the "General comments" 3 by reviewer 1. We have abandoned the scaling approach through comparing the diurnals of organic compounds observed in common with MION-Br and MION-NO₃. Instead, after comparing the ambient sulphuric acid concentrations, we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO₃. This scaling approach is more reasonable since the calibrations were done for sulphuric acid

(compound representing the kinetic limit sensitivity; Viggiano et al., 1997;Berresheim et al., 2000) for MION-Br and MION-NO₃. Besides, we have also added the correlations for several dominant CHO and CHON species (including $C_7H_{10}O_4$, $C_8H_{12}O_4$, $C_{10}H_{15}NO_{6-7}$) discussed in the manuscript in Table S3 for a simplified examination of isomer content for individual compound (see also Table R1).

5. Line 150: The quantification of PTR-TOF is also way too simple. It would be better to use the relationship between the kinetic reaction rate constants (H3O+ with VOCs) and calibrated sensitivity (Sekimoto et al., 2017 IJMS; Yuan et al., 2017 CR).

We thank the reviewer for this suggestion. As the reviewer suggested, the sensitivities of different VOCs measured by PTR-ToF can be calculated from the kinetics of the proton-transfer reactions. The proton-transfer reaction rate constants have only been measured for a few compounds. Sekimoto et al. (2017) showed that the proton-transfer reaction rate constants of various VOCs can be obtained based on the molecular mass, elemental composition, and functionality of VOCs. However, in this study, we provided the quantification of all compounds measured by Vocus PTR-ToF including those compounds with unknown molecular formulae. To assess the uncertainties of our quantification method, we have compared the concentrations of several CH compounds (e.g., sesquiterpenes and diterpenes) as well as several dominant CHO and CHON species (including $C_7H_{10}O_4$, $C_8H_{12}O_4$, and $C_{10}H_{15}NO_{6-7}$ discussed in the manuscript) using our simple quantification method and the kinetic reaction rate constants. The resulting comparison did not show huge differences (slopes between 0.59–0.75; see *Figure R3*) between these two quantification methods. Therefore we prefer to keep the quantification method in the current version of the manuscript. The comparison figure was added as Figure S2. The original Figure S2-S9 are now Figure S3-S11. For clarification, we have added the information in Line 152 (Section 2.2.1, 2nd paragraph) of the manuscript as following: "Quantification using the relationship between the kinetic reaction rate constants and calibrated sensitivity (Sekimoto et al., 2017; Yuan et al., 2017) did not show huge differences (slopes between 0.59–0.75; see Figure S2) for the concentrations of several CH species (e.g., sesquiterpenes and diterpenes) and several dominant CHO and CHON species (e.g., C₇H₁₀O₄, C₈H₁₂O₄, C₁₀H₁₅NO₆₋₇), compared to the above-mentioned quantification method we used. The Vocus [...]".



Figure R3. Comparison for the Vocus quantification based on the kinetic reaction rate constant and calculated sensitivity (Sekimoto et al., 2017; Yuan et al., 2017) vs. the Vocus quantification without using it.

6. Line 160-175: Could the authors comment on the uncertainties form the calculation of volatility from the parameterization method.

Formula-based parameterization is based on volatility properties of functional groups (Donahue et al., 2011). When applied to individual molecules, with the only input being the molecular composition, isomers cannot be differentiated and therefore could induce uncertainties. The error for volatility estimation is expected to be smaller when applied to a mixture of isomers compared to a specific compound (Isaacman-VanWertz and Aumont, 2020), which is typically the case in the complex ambient environment. A clear quantification of the uncertainties arising from the presence of all potential isomers, however, is limited within this dataset. Besides, as mentioned by reviewer 1, the empirical Li et al. (2016) approach was derived with very few organonitrates and therefore could lead to bias for the estimated vapor pressure of CHON compounds (Isaacman-VanWertz and Aumont, 2020). As suggested by reviewer 1, we have modified the Li et al. (2016) parameterization and recalculated the VBS distributions by treating NO₃ units as OH groups following the approach by Daumit et al. (2013) to reduce the uncertainties. Volatility parameterization has been tested quantitatively for terpene oxidation products (including organonitrates) by Wang et al. (2020) using FIGAERO thermal desorption measurements and also tested in particle growth rate closure studies in the CLOUD experiment by Stolzenburg et al. (2018). In both cases the parameterization has been shown to be accurate to within 1 order of magnitude (one decadal volatility bin).

We have updated the Figures and Table (Figure 6, 7, S10, S11, and Table 2), and the corresponding numbers in the texts based on the modified parameterization method. The corresponding information on the modified approach as well as the uncertainties from formula-based parameterization were added to the manuscript as following:

Line 173 (Section 2.2.2, 1st paragraph): "[...] these "b" values can be found in Li et al. (2016). Due to that the empirical approach by Li et al. (2016) derived with very few organonitrates could lead to bias for the estimated vapor pressure (Isaacman-VanWertz and Aumont, 2020), we modified the C_{sat} (298 K) of CHON compounds by replacing all NO₃ groups as OH groups (Daumit et al., 2013)."

Line 179 (Section 2.2.2, 3rd paragraph): "Uncertainties arising from the potential presence of isomers is limited within this dataset, since they cannot be differentiated using the formula-based parameterization with the only input being the molecular composition. Accuracy to within 1 order of magnitude for terpene oxidation products has been confirmed by calibrated thermal desorption measurement (Wang et al., 2020) and by closure with size-resolved growth rate measurements at the CLOUD experiment (Stolzenburg et al., 2018)."

7. Figure 1: why Br CIMS has more data missing than NO3-CIMS, for example the period around May 17, as this is achieved by the same instrument.

The reviewer does have a sharp eye. The MION inlet can be run with only one ion

source if wanted. In this case, we had a problem with the mass flow controller of the Br mode, so we set the instrument measuring only with API mode and NO₃ mode until the problem was fixed. The following information was added to Figure 1 caption (Line 672) for better clarification: "[...] The data gap between MION-Br and MION-NO₃ (e.g., around May 17) was due to that the MION API-ToF was only running with API mode and NO₃ mode because of a mass flow controller issue for Br mode at that time."

8. Line 275-280: can the authors also provide the comparison of time series for some of the important ions. May be also their correlation. It is expected PTR-TOF would measure more species, as almost all OVOCs has signals in the mass spectra with similar sensitivities. It might be due some of the isomers are not measured by Br CIMS and NO3-CIMS.

In addition to the diurnal variations of total CH, total CHO, and total CHON compounds shown in Figure 4, we have also compared the diurnal patterns of several dominant CHO and CHON species (including C₇H₁₀O₄, C₈H₁₂O₄, C₁₀H₁₅NO₆₋₇), which were also found to vary among different measurement techniques (in Line 287-293 and Figure 5). As also stated by the reviewer, it's possibly due to some of the isomers were not detected by MION-Br or MION-NO₃., which was also indicated from the inconsistent trends in time series and the varying correlations for these abovementioned dominant CHO and CHON species (see Figure R4 and Table R1). We have added their time series and correlations as Figure S8 and Table S3 for a simplified examination of isomer content for individual compound. For the modification in the manuscript, we refer to our response in "General comments" 3 by reviewer 1.



Figure R4. Time series of the dominant CHO and CHON species measured by Vocus, *MION-Br*, and *MION-NO*₃.

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