# 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-NO<sub>3</sub>). 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-NO<sub>3</sub> 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, 2<sup>nd</sup> 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<sup>-3</sup>. In general [...]".

Line 348-349 (Section 4, 1<sup>st</sup> 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<sup>-3</sup>. 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 NO<sub>3</sub> 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 NO<sub>3</sub> 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*<sup>3</sup> (See Figure R2a), we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO<sub>3</sub>. The reason why we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO<sub>3</sub> 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-NO<sub>3</sub>. 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, 1<sup>st</sup> paragraph) of the manuscript: "By comparing the ambient  $H_2SO_4$  concentrations measured by MION-Br and MION-NO<sub>3</sub>, the median value (0.53) was used to scale down the H<sub>2</sub>SO<sub>4</sub> 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, 2<sup>nd</sup> 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-NO<sub>3</sub> (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 <sub>3</sub>	MION-Br vs. MION-NO <sub>3</sub>
$C_7 H_{10} O_4$	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, 2<sup>nd</sup> 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, 1<sup>st</sup> 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, 1<sup>st</sup> 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, 1<sup>st</sup> 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, 1<sup>st</sup> 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, 2<sup>nd</sup> 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 (H<sub>2</sub>SO<sub>4</sub>, 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 ( $\Omega$ ) 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, 1<sup>st</sup> 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 10<sup>4</sup> to 10<sup>8</sup> cm<sup>-3</sup> (roughly 10<sup>-3</sup> 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<sup>°</sup>3 or 10<sup>°</sup>2 instead of 10<sup>°</sup>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-NO<sub>3</sub> 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-NO<sub>3</sub>) as we mentioned in Line 155-157 (section 2.2.1, 3<sup>rd</sup> 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, 3<sup>rd</sup> 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<sup>-1</sup>) 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, 1<sup>st</sup> 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<sup>-1</sup>. 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 <sup>81</sup>Br<sup>-</sup> clustered compounds when we fit the <sup>79</sup>Br<sup>-</sup> clustered compounds (also true for e.g. <sup>13</sup>C and <sup>34</sup>S when we fit <sup>12</sup>C-containing or <sup>32</sup>S-containing compounds). Therefore we didn't manually add the <sup>81</sup>Br<sup>-</sup> 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 <sup>81</sup>Br<sup>-</sup> could be separated from  $C_xH_{y+2}O_z$  clustered with <sup>79</sup>Br<sup>-</sup>.

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

Line 110 (Section 2.2.1, 1<sup>st</sup> 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 (<sup>79</sup>Br<sup>-</sup> and <sup>81</sup>Br<sup>-</sup>) share similar relative isotopic abundance, but only the compound clustered with <sup>79</sup>Br<sup>-</sup> 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 ( $\Gamma^-$ ) 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, 2<sup>nd</sup> 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-NO<sub>3</sub>. Instead, after comparing the ambient sulphuric acid concentrations, we scaled the sulphuric acid calibration factor of MION-Br to that of MION-NO<sub>3</sub>. 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-NO<sub>3</sub>. 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, 2<sup>nd</sup> 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., C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>, C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>, C<sub>10</sub>H<sub>15</sub>NO<sub>6-7</sub>), 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 NO<sub>3</sub> 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, 1<sup>st</sup> 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 NO<sub>3</sub> groups as OH groups (Daumit et al., 2013)."

Line 179 (Section 2.2.2, 3<sup>rd</sup> 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 NO<sub>3</sub> 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-NO<sub>3</sub> (e.g., around May 17) was due to that the MION API-ToF was only running with API mode and NO<sub>3</sub> 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 C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>, C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>, C<sub>10</sub>H<sub>15</sub>NO<sub>6-7</sub>), 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-NO<sub>3</sub>., 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*<sub>3</sub>.

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# Information for the editor:

We realized that for Vocus measurements, we had not quantified the organic compounds with authentic standards (including isoprene, monoterpenes, some aromatic compounds, and  $C_4H_6O$ ) based on their sensitivities from direct calibrations in the submitted version of the manuscript. We have now corrected for them. Figures and values involving these Vocus data (i.e. values in the results and discussion part of the manuscript, Figure 1-3, Table 1, and Figure S4-S6 and Table S2 in the SI file) were updated. The correction does not alter results or conclusions in our manuscript in any way.

For the editor's convenience, we show below the contribution of different compound groups (Table E1 and E2), time series of total organics (Figure E1), contribution of CHOX compounds with different number of oxygen atoms to total CHOX compounds (Figures E2), and contribution of organic compounds with different number of oxygen atoms to sum of CHOX and CHX compounds (Figure E3) measured by Vocus before and after the correction.

Compound group	Before the correction	After the correction
СН	<i>31.8</i> ± <i>15.3</i> %	35.2 ± 15.1 %
СНО	45.9 ± 9.5 %	43.6 ± 9.4 %
CHON	8.5 ± 2.7 %	8.1 ± 2.7 %
others	13.8 ± 3.9 %	13.1 ± 3.9 %

*Table E1.* Contribution (%, average  $\pm 1$  standard deviation) of different compound groups to total organics measured by Vocus before and after the correction.

**Table E2.** Sum contribution (%, average  $\pm 1$  standard deviation) of  $C_xH$ ,  $C_xHO$ , and  $C_xHON$  groups (x = 5, 10, 15, and 20) to total CH, CHO and CHON compounds measured by Vocus before and after the correction.

Compound group	Before the correction	After the correction
C <sub>x</sub> H/CH	35.5 ± 11.3 %	38.3 ± 12.5 %
C <sub>x</sub> HO/CHO	27.3 ± 3.2 %	27.4 ± 3.2 %
C <sub>x</sub> HON/CHON	16.2 ± 2.3 %	16.2 ± 2.3 %



*Figure E1. Time series of total gaseous organics measured by Vocus before and after the correction.* 



*Figure E2.* Contribution of measured CHOX compounds with different number of oxygen atoms to total CHOX compounds as a function of the number of carbon atoms for Vocus *before (a)* and *after (b)* the correction.



**Figure E3.** Contribution of organic compounds with different number of oxygen atoms to all organic compounds (including CHX compounds) as a function of the number of carbon atoms measured by Vocus **before (a)** and **after (b)** the correction.

# 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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Abstract. The molecular composition and volatility of gaseous organic compounds were investigated during 15 April-July 2019 at the Station for Measuring Ecosystem - Atmosphere Relations (SMEAR) II situated in a boreal forest in Hyytiälä, southern Finland. 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 proton-transferreaction time-of-flight mass spectrometer (Vocus PTR-ToF; hereafter Vocus) was deployed to measure volatile 20 organic compounds (VOCs) and less oxygenated VOCs (i.e., OVOCs). In addition, a multi-scheme chemical ionization inlet coupled to an atmospheric pressure interface time-of-flight mass spectrometer (MION APiAPI-ToF) was used to detect less oxygenated VOCs (using Br<sup>-</sup> as the reagent ion; hereafter MION-Br) and more oxygenated VOCs (including highly oxygenated organic molecules, HOMs; using NO<sub>3</sub><sup>-</sup> as the reagent ion; hereafter MION-NO<sub>3</sub>). The comparison among different measurement techniques revealed that the highest 25 elemental oxygen-to-carbon ratios (O:C) of organic compounds were observed by the MION-NO<sub>3</sub> ( $0.9 \pm 0.1$ , average  $\pm 1$  standard deviation), followed by the MION-Br (0.8  $\pm$  0.1); and lowest by Vocus (0.2  $\pm$  0.1). Diurnal patterns of the measured organic compounds were found to vary among different measurement techniques, even for compounds with the same molecular formula, suggesting contributions of different isomers detected by the different techniques and/or fragmentation from different parent compounds inside the instruments. Based on the 30 complementary molecular information obtained from Vocus, MION-Br, and MION-NO3, a more complete picture of the bulk volatility of all measured organic compounds in this boreal forest was obtained. As expected, the VOC class was the most abundant (about 49.4-53.2%), followed by intermediate-volatility organic compounds (IVOC, about 48.945.9 %). Although condensable organic compounds (low-volatility organic compounds, LVOC; extremely low-volatility organic compounds, ELVOC; and ultralow-volatility organic compounds, ULVOC) only 35 comprised about 0.30.2 % of the total gaseous organic compounds, they play an important role in new particle formation as shown in previous studies in this boreal forest. Our study shows the full characterization of the gaseous organic compounds in the boreal forest and the advantages of combining Vocus and MION APiAPI-ToF for measuring ambient organic compounds with different oxidation extent (from VOCs to HOMs). The results therefore provide a more comprehensive understanding of the molecular composition and volatility of atmospheric organic compounds as well as new insights in interpreting ambient measurements or testing/improving parameterizations in transport and climate models.

#### 1 Introduction

Organic aerosol (OA) has significant impacts on climate (IPCC, 2013), air quality (Boers et al., 2015), and human health (Nel, 2005;Rückerl et al., 2011). Large amounts of biogenic and anthropogenic volatile organic compounds 45 (VOCs) are emitted into the atmosphere (Atkinson and Arey, 2003), with biogenic VOCs (BVOCs) emissions greatly surpassing anthropogenic VOC emissions globally (Heald et al., 2008). The global BVOC emissions are dominated by terpenes (isoprene ( $C_5H_8$ ), 594 Tg C a<sup>-1</sup>; monoterpenes ( $C_{10}H_{16}$ ), 95 Tg C a<sup>-1</sup>; and sesquiterpenes  $(C_{15}H_{24})$ , 20 Tg C a<sup>-1</sup>) (Sindelarova et al., 2014), which are mainly emitted by vegetation and can be influenced by meteorological conditions, such as temperature and light (Guenther et al., 1995;Kaser et al., 2013). After emission, 50 they can undergo gas-phase oxidation with ozone (O<sub>3</sub>), hydroxyl radical (OH), or nitrate radical (NO<sub>3</sub>) forming thousands of oxygenated VOCs (i.e., OVOCs) with diverse functionalities that can be grouped into different volatility classes; Intermediate-volatility (IVOC), semi-volatile (SVOC), low-volatility (LVOC), extremely lowvolatility (ELVOC), and ultralow-volatility (ULVOC). Organic compounds with sufficiently low volatility (e.g., LVOC, ELVOC, and ULVOC) can either form new particles or partition into the particle phase contributing to 55 particulate growth and mass (Ehn et al., 2014;Bianchi et al., 2016;Bianchi et al., 2019;Simon et al., 2020;Schervish and Donahue, 2020;Kulmala et al., 2013). Recent studies have shown that highly oxygenated organic molecules (HOMs; Bianchi et al., 2019) are a major source of condensing or nucleating compounds and they play an important role in atmospheric new particle formation (Ehn et al., 2014;Bianchi et al., 2016;Kirkby et al., 2016;Tröstl et al., 2016;Bianchi et al., 2019;Kulmala et al., 1998). However, as a result of the complexity and analytical challenges 60 of the precursor VOCs as well as the chemical composition and physicochemical properties of the resulting

oxidation products (i.e., OVOCs), skill predicting their effects on air quality and climate is still limited. Mass spectrometric techniques represent one general approach to investigate the chemical composition of organic compounds (Sullivan and Prather, 2005;Nash et al., 2006). One common ionization technique used in

aerosol research is chemical ionization (CI; e.g., Caldwell et al., 1989;Ehn et al., 2014;Lopez-Hilfiker et al., 2014;Huang et al., 2019a). It is a soft ionization method (Gross, 2017) that utilizes the reactivity of the analyte towards the reagent ion to ionize molecules via transfer of an electron, proton, or other ions such as bromide and nitrate (Caldwell et al., 1989;Ehn et al., 2014;Sanchez et al., 2016;Yuan et al., 2017;Krechmer et al., 2018). Different chemical ionization mass spectrometers (CIMS) have different capabilities and sensitivities for detecting organic compounds (Riva et al., 2019). Proton-transfer-reaction mass spectrometry (PTR-MS) has been widely used to measure VOCs in the atmosphere (Yuan et al., 2017). The recently developed Vocus PTR time-of-flight mass spectrometer (Vocus PTR-ToF) has greatly enhanced sensitivity due to a newly designed chemical ionization source (Krechmer et al., 2018), and can detect a broader spectrum of VOCs (even diterpenes) and their oxygenated products (up to 6 to 8 oxygen atoms for monoterpene oxidation products; Li et al., 2020b). However, Vocus PTR-

ToF is not the best optionpreferred for detecting HOMs or dimers (Li et al., 2020b;Riva et al., 2019)., The potential

- 75 reason for the latter case could be resulted from possibly due to the fragmentation inside the transferring between the inlet and the detector of the instrument (Heinritzi et al., 2016) and/or losses in the sampling lines and on the walls of the inlet (Riva et al., 2019). The detection of less oxygenated VOC<sub>S</sub> (including less oxygenated dimers) and more oxygenated VOCs (including HOMs) can be well achieved by another instrument: an Atmospheric Pressure interface Interface Time-of-Flight mass spectrometer (APiAPI-ToF) coupled to a novel chemical
- 80 ionization inlet, Multi-scheme chemical IONization inlet (MION; Rissanen et al., 2019).; +Via the fast switching between multiple reagent ion schemes (e.g., i.e., bromide and nitrate), It has been found that MION APIAPI-ToF is able to provide a more complete picture of the OVOCs for laboratory experiments performed in flow tube reactors (Rissanen et al., 2019). 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

- 85 detection of hydroperoxyl radicals (Sanchez et al., 2016) and peroxy radicals formed by autoxidation (Rissanen et al., 2019). In addition to the molecular composition of organic compounds itself provided by the abovementioned state-of-the-art instruments (i.e., Vocus PTR-ToF and MION APiAPI-ToF), these information can also be used in volatility parameterizations to calculate effective saturation mass concentrations ( $C_{sat}$ ) of individual organic compounds (Li et al., 2016;Donahue et al., 2011;Mohr et al., 2019), which can be then grouped into different
- 90 volatility classes (or bins), i.e., volatility basis sets (VBS; e.g., Donahue et al., 2006;2011;2012;Cappa and Jimenez, 2010). However, due to the different instrumental capabilities and sensitivities as well as the lack of calibration standards for the majority of organic compounds for the different measurement techniques as abovementioned, 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.

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In the present work, we investigate the chemical composition and volatility of gaseous organic compounds (VOCs and OVOCs) measured during April and July 2019 in a boreal forest in Hyytiälä, southern Finland. The capabilities of the recently developed MION APiAPI-ToF for measuring ambient OVOCs are reported for the first time. Besides, the molecular composition and volatility of the OVOCs measured by MION APiAPI-ToF are compared and complemented with those as well as their precursor VOCs observed with Vocus PTR-ToF. With the combination of the organic compounds measured by both instruments, we present a more comprehensive picture of the molecular composition and volatility of the gaseous organic compounds in this boreal forest.

#### 2 Methodology

#### 2.1 Site description

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The measurements were conducted between April 16–July 26, 2019 at the University of Helsinki Station for Measuring Ecosystem – Atmosphere Relations (SMEAR) II (Hari and Kulmala, 2005), which is located in a boreal forest in Hyytiälä, southern Finland (61°51'N, 24°17'E, 181 m a.s.l.). This station is dominated by Scots pine (Pinus sylvestris), and monoterpenes are found to be the dominating emitted biogenic non-methane VOCs (Barreira et al., 2017;Hakola et al., 2012). The measurement station has been considered as a rural background site (Manninen et al., 2010; Williams et al., 2011), and the nearest big city is Tampere, with more than 200,000 inhabitants and located ~60 km in the SW of our measurement site. A sawmill which is located 6-7 km away to

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the SE of our measurement site can contribute significantly to the OA loading in the case of SE winds, and the

sawmill OA composition has been found to resemble biogenic OA a lot (Liao et al., 2011;Äijälä et al., 2017;Heikkinen et al., 2020).

#### 2.2 Measurements, quantification, and volatility calculation of gaseous organic compounds

All mass spectrometers were set up in a temperature-controlled measurement container kept at ~25 °C. Sampling
 inlets were located about 1.5 m a.g.l. All data are reported in Finnish winter time Eastern European Time (UTC+2).

#### 2.2.1 Measurements and quantification of gaseous organic compounds

- An APiAPI-ToF (Tofwerk Ltd.: equipped with a long ToF with a mass resolving power of ~9000) equipped withcoupled to a recently developed multi-scheme chemical ionization inlet (MION, Karsa Ltd.; Rissanen et al., 2019) was used to analyze the molecular composition of OVOCs at a time resolution of 30 min. During the 30-min cycles of measurements, MION APiAPI-ToF switched modes among nitrate (NO<sub>3</sub><sup>-</sup>, 8 min), bromide (Br<sup>-</sup>, 8 min), and APi-API (measuring natural ions, 10 min) modes, followed by 2 min of zeroing before switching from APi-API mode to the next mode. More details about the instrument are well described by Rissanen et al. (2019). 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<sup>-1</sup>. Due to the large inlet diameter and flow rate, the SVOC and HOM losses are expected to be insignificant. Through the fast switching between the two reagent ion schemes, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, less oxygenated VOCs (including less oxygenated dimers) and more oxygenated VOCs (including HOMs) can be measured, respectively (Rissanen et al., 2019). Data were analysed with the software packages, "tofTools" (developed by Junninen et al. (2010)) and "Labbis" (developed by Karsa Ltd.), which run in the MATLAB environment
- 130 (MathWorks Inc., USA). Hereafter results from these two reagent ion schemes are abbreviated as MION-Br and MION-NO<sub>3</sub>. The quantification of gaseous organic compounds measured with MION-Br and MION-NO<sub>3</sub> was calculated as in equation (1) and (2), respectively:

$$[\text{org}] = \frac{\text{org}(\text{Br}^{-})}{\text{Br}^{-} + \text{H}_2 \text{O}(\text{Br}^{-})} \times C_{Br^{-}},$$
(1)  
$$[\text{org}] = \frac{\text{org}(\text{NO}_3)}{\sum_{i=0}^{2} (\text{HNO}_3)_i (\text{NO}_3^{-})} \times C_{\text{NO}_3^{-}}.$$
(2)

where [org] is the concentration (unit: cm<sup>-3</sup>) of the gaseous organic compound (obtained from high resolution 135 fitting of each nominal mass) to be quantified; the numerators on the right-hand side are its detected signal clustered with bromide or nitrate, and the denominators are the sum of the reagent ion signals;  $C_{Br}$  and  $C_{NO_3}$  are the calibration factors representing the sensitivity of organic compound. The two stable isotopes of bromide (<sup>79</sup>Br<sup>-</sup> and  $^{81}$ Br<sup>-</sup>) share similar relative isotopic abundance, but only the compound clustered with  $^{79}$ Br<sup>-</sup> was used for the 140 quantification (Sanchez et al., 2016), as the calibration factor,  $C_{Br^-}$ , was also calculated in a similar way. Following the approach by Rissanen et al. (2019), the calibration factors,  $C_{Br^-}$  and  $C_{NO_3^-}$ , for sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) compound representing the kinetic limit sensitivity; Viggiano et al., 1997; Berresheim et al., 2000) were determined to be  $2.33 \times 10^{11}$  cm<sup>-3</sup> and  $4.68 \times 10^{10}$  cm<sup>-3</sup>, respectively. The calibration factors are higher than those reported by Rissanen et al. (2019) due to different instrumental settings and inlet setup. By comparing the ambient 145 H<sub>2</sub>SO<sub>4</sub> concentrations measured by MION-Br and MION-NO<sub>3</sub>, the median value (0.53) was used to scale down the H<sub>2</sub>SO<sub>4</sub> 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). With the maximum sensitivity applied, the concentrations therefore represent a lower limit. The uncertainties in the measured organic compound

concentrations using calibration factors for  $H_2SO_4$  have been reported to be  $\pm 50$  % (Ehn et al., 2014) or a factor of

2 (Berndt et al., 2015). However, the uncertainties could be higher with variations in e.g. temperature and relative humidity (RH) in the field. Therefore, based on the concentrations of measured organic compounds in common for MION Br and MION NO<sub>3</sub> (see Figure S1), 230 compounds out of 269 compounds were found to have similar diurnal behaviors and they were likely to be the same species (i.e., possibly not isomers). By comparing their individual concentrations measured by MION Br vs. MION NO<sub>3</sub>, the median value (0.3) was used to scale down the concentrations of all organic compounds measured by MION-Br.

A Vocus PTR-ToF (Aerodyne Research Inc.; hereafter Vocus) was deployed to measure VOCs and less oxygenated VOCs at a time resolution of 5 s. During the measurements, the Vocus ionization source was operated at a pressure of 1.5 mbar. The ambient air was sampled via a polytetrafluoroethylene (PTFE) tube of ca. 1 m length and a total sample flow of 4.5 L min<sup>-1</sup>. Of the total sample flow, around 100–150 cm<sup>3</sup> min<sup>-1</sup> went into the Vocus and the remainder was directed to the exhaust. The Vocus was automatically calibrated every three hours using a multi-component standard cylinder. The standard gases were diluted by the injection of zero air with a built-in active carbon filter, producing the VOCs mixing ratio of around 5 ppb. The sensitivity of VOCs measured by PTR instruments has been shown to relate to their elemental composition and functionality (Sekimoto et al., 2017). Some compounds were calibrated using authentic standards, including isoprene, monoterpenes, and some aromatic

- 165 compounds. Compounds without authentic standards were divided into four different molecular groups, the CH (compounds with only carbon and hydrogen atoms), CHO (compounds with only carbon, hydrogen, and oxygen atoms), CHON (compounds with only carbon, hydrogen, oxygen, and nitrogen atoms), and others. Compounds with the formula of CH and CHO were quantified with the average sensitivities of the standards CH and CHO, respectively. For the groups of CHON and others, there was no standard available in the calibration mixture. We
- 170 used the average sensitivity of all the CH and CHO standards to quantify CHON compounds and others. 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., C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>, C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>, and C<sub>10</sub>H<sub>15</sub>NO<sub>6-7</sub>), compared to the above-mentioned quantification
- 175 <u>method we used.</u> The Vocus data analysis was performed using the software package "Tofware" (provided by Tofwerk Ltd.) that runs in the Igor Pro environment (WaveMetrics Inc., USA). 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.
- 180 When combining the organic compounds measured by the three different ionization techniques (i.e., MION-Br, MION-NO<sub>3</sub>, and Vocus), for organic compounds observed in all ionization techniques the highest concentration was used. Background subtraction was performed for all spectra and therefore a lower signal for the same compound detected by any of the ionization techniques suggests a lower ionisation efficiency of the corresponding method (Stolzenburg et al., 2018).

#### 185 2.2.2 Volatility calculation of gaseous organic compounds

Effective saturation mass concentrations ( $C_{sat}$ ), a measure for volatility of a compound, were parameterized for each organic compound using the approach by Li et al. (2016) as in equation (3):

 $\log_{10} C_{\text{sat}} (298 \text{ K}) = (n_{\text{C}}^0 - n_{\text{C}}) b_{\text{C}} - n_0 b_0 - 2 \frac{n_{\text{C}} n_0}{(n_{\text{C}} + n_0)} b_{\text{CO}} - n_{\text{N}} b_{\text{N}} - n_{\text{S}} b_{\text{S}}$ (3)

where  $n_{\rm C}$ ,  $n_{\rm N}$ ,  $n_{\rm N}$ , and  $n_{\rm S}$  are the number of carbon, oxygen, nitrogen, and sulfur atoms in the organic compound,

- 190 respectively;  $n_{\rm C}^0$  is the reference carbon number;  $b_{\rm C}$ ,  $b_{\rm O}$ ,  $b_{\rm N}$ , and  $b_{\rm S}$  are the contribution of each atom to  $\log_{10}C_{\rm sat}$ , respectively;  $b_{\rm CO}$  is the carbon–oxygen nonideality (Donahue et al., 2011). These "b" values depend on the composition of precursor gases, depending largely on whether the precursors are aliphatic (including terpenes) or aromatic. In addition to being derived from literature structure activity relations (i.e., SIMPOL; Pankow and Asher, 2008), the relations have been quantitatively confirmed for both aliphatic and aromatic systems using filter inlet
- for gases and aerosols (FIGAERO) thermal desorption CIMS measurements on carefully controlled precursor oxidation experiments at the CLOUD (Cosmics Leaving Outdoor Droplets) facility at CERN (European Organization for Nuclear Research) (Ye et al., 2019;Wang et al., 2020). For the boreal forest conditions in this work we use the aliphatic (more volatile) parameterization and 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<sub>sat</sub>* (298 K) of CHON compounds by replacing all NO<sub>3</sub> groups as OH groups (Daumit et al., 2013).

To obtain the  $C_{sat}$  (T), we adjusted the  $C_{sat}$  (298 K) (Donahue et al., 2011;Epstein et al., 2010) to the measured ambient temperature as in equations (4) and (5):

$$\log_{10} C_{\text{sat}} (T) = \log_{10} C_{\text{sat}} (298 \text{ K}) + \frac{\Delta H_{\text{vap}}}{R\ln(10)} \left(\frac{1}{298} - \frac{1}{T}\right), \tag{4}$$

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$$\Delta H_{\rm vap}(kJ\,{\rm mol}^{-1}) = -11 \cdot \log_{10} C_{\rm sat}(298\,{\rm K}) + 129.$$
 (5)

where *T* is the temperature in Kelvin;  $C_{\text{sat}}$  (298 K) is the saturation mass concentrations at 298 K;  $\Delta H_{\text{vap}}$  is the vaporization enthalpy; *R* is the gas constant (8.3143 J K<sup>-1</sup> mol<sup>-1</sup>).

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). Besides, the fragmentation of organic compounds inside the instruments (e.g., Vocus) may also bias the C<sub>sat</sub> results towards higher volatilities (Heinritzi et al., 2016).

#### 2.3 Additional co-located measurements

- 215 The meteorological parameters were continuously monitored at this measurement site. Temperature was monitored with a Pt100 sensor (Platinum resistance thermometer with a resistance of 100 ohms (Ω) at 0 °C) inside ventilated custom-made radiation shield, while wind directions and wind speed with a 2D Ultrasonic anemometer (Adolf Thies GmbH & Co. KG), and the global radiation with an EQ08 pyranometer (Carter-Scott Manufacturing Pty. Ltd.). The main wind direction above the canopy during the measurement period was southwest (see Figure S2S3).
- 220 The mixing ratios of ozone (O<sub>3</sub>) and nitrogen oxides (NO and NO<sub>2</sub>) were measured with an ultraviolet light absorption analyzer (TEI 49C, Thermo Fisher Scientific Inc.) and a chemiluminescence analyzer (TEI 42CTL, Thermo Fisher Scientific Inc.), respectively. The mixing ratios of sulfur dioxide (SO<sub>2</sub>) were measured with a fluorescence analyzer (TEI 43CTL, Thermo Fisher Scientific Inc.).

An aerosol chemical speciation monitor (ACSM; Aerodyne Research Inc.; Ng et al., 2011) was deployed to continuously measure the non-refractory sub-micrometer aerosol particle chemical composition. The ACSM,
which contains a quadrupole mass spectrometer, provided unit-mass resolution mass spectra every 30 min. This information was chemically speciated to organic, sulfate, nitrate, ammonium, and chloride concentrations by the ACSM analysis software. The mass concentrations of each species were calculated based on frequently conducted ionization efficiency calibrations. The data were corrected for collection efficiency, which was ca. 60 % during

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the measurement period. The sampling was conducted through a  $PM_{2.5}$  cyclone and a Nafion dryer (RH < 30 %) with a stainless steel tube of ca. 3 m length and a flow rate of  $3 \text{ L min}^{-1}$  (only 1.4 cm<sup>3</sup> s<sup>-1</sup> into the ACSM). The recorded data were analyzed using the ACSM local v. 1.6.0.3 toolkit (provided by Aerodyne Research Inc.) within the Igor Pro v. 6.37 (Wavemetrics Inc., USA). More details about ACSM operation and data processing can be found in Heikkinen et al. (2020).

#### 235 **3 Results and discussion**

## 3.1 Overview of the measurements

Figure 1 shows the overview of the time series of meteorological parameters (temperature, global radiation, and wind direction and wind speed), trace gas concentrations (SO<sub>2</sub>, O<sub>3</sub>, NO, and NO<sub>2</sub>), and total gaseous organic compounds measured by MION-Br, MION-NO<sub>3</sub>, and Vocus, as well as total particulate organics measured by 240 ACSM. Note that relatively long-lived compounds like methanol, 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). As we can see from Figure 1a, most of the measurement days had strong photochemical activity with ambient temperature exhibiting clear diurnal patterns ranging between -3 and 32 °C. 245 In general, the time series of the total organics (both gas phase and particle phase; see Fig. 1e-f) measured by MION-Br, MION-NO<sub>3</sub>, Vocus, and ACSM were similar during the measurement period. Elevated levels of total gaseous and particulate organics (e.g., May 17-24 and June 7-10; see Fig. 1e-f) were observed at warmer days with strong global radiation and the main wind direction coming from southeast (the direction of the sawmill; for e.g. May 17-24) or southwest (for e.g. June 7-10; see Fig. 1a-b). Besides, higher concentrations of oxidants of 250 VOCs (such as  $O_3$ ) and/or anthropogenic pollutants (such as  $SO_2$  and  $NO_x$ ) also followed some of the elevated concentrations of gaseous and/or particulate organics (e.g., April 19-May 3, May 17-24, and June 7-10; see Fig. 1c-d). The observations of the elevated organics could be resulted from higher VOC emissions (e.g., terpenes, the typically observed VOCs, Li et al., 2020a; Figure \$3\$4) influenced by meteorological conditions (i.e., temperature and/or light; Guenther et al., 1995;Kaser et al., 2013), different air mass origins (e.g., terpene pollutions from the 255 sawmill in the case of SE winds; Liao et al., 2011; Äijälä et al., 2017; Heikkinen et al., 2020), as well as chemistry initiated by/related with different trace gases (Yan et al., 2016;Massoli et al., 2018;Huang et al., 2019b;Heikkinen et al., 2020). The results suggest the important roles meteorological parameters, trace gases, and air masses play in the emission and oxidation reactions of organic compounds. Due to the soft ionization processes of organic molecules in the Vocus, MION-Br, and MION-NO<sub>3</sub>, molecular composition of organic compounds was obtained. 260 In the next section we will discuss the molecular composition of gaseous organic compounds measured by Vocus, MION-Br, and MION-NO<sub>3</sub>.

#### 3.2 Molecular composition of gaseous organic compounds

During the measurement period, Vocus identified 72 CH compounds  $(C_{x\geq 1}H_{y\geq 1})$  and 431 CHOX compounds  $(C_{x\geq 1}H_{y\geq 1}O_{z\geq 1}X_{0-n})$ , with X being different atoms like N, S, or a combination thereof, while MION-Br and MION-

- 265 NO<sub>3</sub> detected 567 and 687 CHOX compounds, respectively. Substantial overlaps of organic compounds were observed for these three ionization techniques while distinct organic compounds were also detected with individual method (Figure S1). The average mass-weighted chemical compositions for organic compounds measured by Vocus, MION-Br, and MION-NO<sub>3</sub> were C<sub>5.3</sub>H<sub>7.5</sub>O<sub>1.1</sub>N<sub>0.1</sub>, C<sub>6.7</sub>H<sub>10.7</sub>O<sub>4.3</sub>N<sub>0.3</sub>, and C<sub>7.5</sub>H<sub>11.4</sub>O<sub>5.4</sub>N<sub>0.3</sub>, respectively. We stress here that the fragmentation of organic compounds inside the Vocus may bias the chemical composition
- 270 <u>towards shorter carbon backbone.</u> And the average mass-weighted chemical composition representing the bulk of all measured <u>gaseous</u> organic compounds (with the approach described in section 2.2.1) in this boreal forest was calculated to be  $C_{6.0}H_{8.7}O_{1.2}N_{0.1}$ , indicative of the short carbon backbone and relatively low oxidation extent. Similar to previous laboratory results (Riva et al., 2019), MION-NO<sub>3</sub> observed the most oxidized compounds with the highest elemental oxygen-to-carbon ratios (O:C;  $0.9 \pm 0.1$ , average  $\pm 1$  standard deviation), followed by the
- 275 MION-Br ( $0.8 \pm 0.1$ ); the O:C of the organics detected by Vocus were lowest ( $0.2 \pm 0.1$ ). In addition, CHO group comprised the largest fraction of the total organic compounds (Vocus:  $45.943.6 \pm 9.45$  %; MION-Br: 75.4 ± 5.3 %; MION-NO<sub>3</sub>: 71.8 ± 7.9 %; see Table 1). The followed bysecond most abundant group for Vocus was CH group making up  $31.835.2 \pm 15.13$  % of its total organic compounds; while it was CHON group for MION-Br (24.1 ± 5.2 %) and MION-NO<sub>3</sub> (28.1 ± 7.9 %; see Table 1), indicating active NO<sub>x</sub> or NO<sub>3</sub> radical related chemistry (Yan
- et al., 2016). CHON group only accounted for  $8.\frac{15}{2} \pm 2.7$  % of the total organic compounds measured by Vocus, possibly due to its lower sensitivity towards larger organonitrates (see also Fig. <u>\$4\$5</u>) caused by their losses in the sampling lines and on the walls of the inlet (Riva et al., 2019) and/or fragmentation inside the instrument (Heinritzi et al., 2016).

The mass defect plots for organic compounds measured by Vocus, MION-Br, and MION-NO3 are shown in 285 Figure 2. Similar to previous studies (e.g., Yan et al., 2016;Li et al., 2020a), multiple series of organic compounds with different number of carbon atoms (such as  $C_5$ ,  $C_{10}$ ,  $C_{15}$ , and  $C_{20}$ ) and oxygen atoms (up to 20; see also Fig. \$4\$5) were measured in this boreal forest environment. Organics with the lowest oxidation extent were better observed by Vocus, while organics with the largest molecular weights and highest oxidation extent were better observed by MION-NO<sub>3</sub> (Fig. 2a). Figure 2b shows the mass defect plots of organic compounds grouped into 290 different categories. The markers are color-coded with different compound groups, such as CH, CHO, CHON, and others. The size of the markers is proportional to the logarithm of the concentration of each compound. Generally, similar to previous laboratory results (Riva et al., 2019; Rissanen et al., 2019), Vocus and MION-Br detected better the CHO compounds in the mass range of 50-100 Da and CHON compounds in the mass range of 50-150 Da, and MION-Br even CHON compounds in the mass range of 350-425 Da, which are most likely to be less oxygenated 295 monomers or dimers; while MION-NO3 was more sensitive towards the CHO and CHON compounds in the mass range of 425–600 Da, which are most likely to be more oxygenated HOM dimers (see Fig. 2b and Fig. S4S5).

We further investigated the contributions of the measured CHOX compounds with different number of oxygen atoms per molecule to total CHOX compounds as a function of the number of carbon atoms (Figure 3). Organic compounds which were detected with higher sensitivity by Vocus were those with the number of carbon atoms
between 3 and 10 and the number of oxygen atoms between 1 and 3 (i.e., less oxygenated monomers); compounds with larger number of carbon atoms (i.e., >10) and oxygen atoms (i.e., >3) were much better detected by MION-Br and MION-NO<sub>3</sub>; the former particularly for CHON compounds with the number of carbon atoms between 15 and 20 and oxygen atoms between 4 and 8 (i.e., larger less oxygenated monomers and dimers; see Fig. <u>S4bS5b</u>)

and the latter particularly for compounds with the number of oxygen atoms larger than 9 (i.e., HOM monomers and dimers; Rissanen et al., 2019;Riva et al., 2019;Li et al., 2020b; see Fig. 3 and Fig. S4S5). In the MION-Br and MION-NO<sub>3</sub> data, CHOX compounds with the number of carbon atoms of 5, 10, 15, and even 20 exhibited relatively elevated contributions compared to their neighbours (Fig. 3), indicating contributions of their potential corresponding precursors, i.e., isoprene, monoterpenes, sesquiterpenes, and diterpenes (together accounting for  $38.35.5 \pm 12.51.3$  % of total CH compounds; see Table S4S2, Fig. S3S4, and Fig. S5S6). 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). Similar pattern was also observed by Huang et al. (2019a) in a rural area in southwest Germany, based on filter inlet for gases and aerosols high-resolution time-of-flight chemical ionization mass spectrometer (FIGAERO-HR-ToF-CIMS) data. The consistency and complement of the results demonstrate the different capabilities of these instruments for measuring gaseous organic compounds with different oxidation extent (from VOCs to HOMs).

3.3 Diurnal characteristics of gaseous organic compounds

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Median diurnal variations of total CH, total CHO, and total CHON compounds measured by Vocus, MION-Br, and MION-NO<sub>3</sub> are shown in Figure 4. In general, the CH and CHO group measured by Vocus exhibited higher levels during the night (see Fig. 4a-b), mainly driven by the boundary layer height dynamics (Baumbach and Vogt, 320 2003;Zha et al., 2018). Besides, CHO compounds measured by Vocus were dominated by O1-2 compounds (see Fig. 3 and Fig. <u>\$4\$5</u>) and 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). In contrast, the CHO and CHON group measured by MION-Br and MION-NO<sub>3</sub> 325 exhibited higher levels during the day (see Fig. 4b), due to strong photochemical oxidation caused by different meteorological parameters (i.e., temperature and global radiation; see Fig. 1a and Fig. S6S7) and/or elevated trace gas levels (e.g., O3 and SO2; see Fig. 1c and Fig. S6S7; Yan et al., 2016; Massoli et al., 2018; Huang et al., 2019b;Bianchi et al., 2017). However, the CHON group measured by Vocus showed relatively stable signals throughout the day (see Fig. 4c). The potential reason could be that the immediate (local) formation effects were 330 smeared out in time as a result of both the reaction of organic peroxy radicals (RO<sub>2</sub>) with NO as well as nighttime NO<sub>3</sub> radical chemistry (see Fig. S6; Yan et al., 2016). 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 335 molecules (mostly peak at night or early morning) and comparatively more oxygenated CHON molecules (mostly peak during daytime) (Li et al., 2020b).

Different diurnal patterns among different measurement techniques can also be found for individual organic compounds with the same molecular formula, such as several dominant CHO and CHON species,  $C_7H_{10}O_4$ (molecular formula corresponding to 3,6-oxoheptanoic acid identified in the laboratory as limonene oxidation product by Faxon et al., 2018;Hammes et al., 2019),  $C_8H_{12}O_4$  (molecular formula corresponding to terpenylic acid identified in monoterpene oxidation product by Zhang et al., 2015;Hammes et al., 2019), and  $C_{10}H_{15}NO_{6-7}$ (identified in the laboratory as monoterpene oxidation products by Boyd et al., 2015;Faxon et al., 2018; see Figure 5). 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 OVOCs with varying oxidation extent, like the terpenerelated C<sub>x</sub>HO and C<sub>x</sub>HON compounds (x = 5, 10, 15, and 20; see Figure. S7S9), which in total accounted for up to 27 % and 39 % of their corresponding CHO and CHON groups (see Table S1S2). Most of the terpene-related C<sub>x</sub>HO(N) groups (x = 5, 10, 15, and 20) with different oxidation extent behaved similar among different measurement techniques, but some were also found to vary (see Fig. S7S9). This can be likely resulted from contributions of compounds with same number of carbon and oxygen atoms but different hydrogen atoms (i.e., different saturation level), different isomers detected by the different techniques, and/or fragmentation products from different parent compounds inside the instruments (e.g., Heinritzi et al., 2016;Zhang et al., 2017).

The results indicate that organic compounds may behave differently among different measurement techniques during different time period. In the next section, we will investigate the volatility of these gaseous organic compounds, which can influence their lifetime and roles in the atmosphere.

### 3.4 Volatility of organic compounds

Based on the  $\log_{10}C_{sat}$  values of all organic compounds parameterized with the approach of modified Li et al. (2016) approach (Daumit et al., 2013; Isaacman-VanWertz and Aumont, 2020) described in section 2.2.2, they were grouped into a 25-bin volatility basis set (VBS; Donahue et al., 2006) (Figure 6a). Organic compounds with  $C_{\rm sat}$ 360 lower than  $10^{-8.5} \,\mu g \,\mathrm{m}^{-3}$ , between  $10^{-8.5} \,\mathrm{and} \, 10^{-4.5} \,\mu g \,\mathrm{m}^{-3}$ , between  $10^{-0.5} \,\mu g \,\mathrm{m}^{-3}$ , between  $10^{-0.5} \,\mathrm{and} \, 10^{-0.5} \,\mathrm{m}^{-3}$ .  $10^{2.5} \,\mu g \text{ m}^{-3}$ , between  $10^{2.5} \text{ and } 10^{6.5} \,\mu g \text{ m}^{-3}$ , and higher than  $10^{6.5} \,\mu g \text{ m}^{-3}$  are termed ULVOC, ELVOC, LVOC, SVOC, IVOC, and VOC, respectively (Donahue et al., 2009;Schervish and Donahue, 2020). The VBS resulting pie charts for these compound groups and their mean contributions are shown in Figure 6b-d and Table 2. Organic compounds with  $C_{\text{sat}}$  of 10<sup>4</sup> µg m<sup>-3</sup> made up the biggest mass contributions for MION-Br and MION-NO<sub>3</sub>, and the 365 dominating  $C_{\text{sat}}$  bin measured by Vocus was organic compounds with  $C_{\text{sat}}$  of 10<sup>6</sup> µg m<sup>-3</sup> (see Fig. 6a). Furthermore, Vocus observed much higher contributions of VOC with  $C_{\text{sat}}$  higher than  $10^8 \,\mu\text{g m}^{-3}$ , whereas MION-NO<sub>3</sub> higher contributions of ELVOC and ULVOC with  $C_{\text{sat}}$  lower than  $10^{-8} \,\mu\text{g}\,\text{m}^{-3}$  (See Fig. 6a). And MION-Br and MION-NO<sub>3</sub> observed comparable contributions of compounds with  $C_{\text{sat}}$  between  $10^{-26}$  and  $\frac{10^4 10^7}{10^7} \,\mu\text{g m}^{-3}$ . We stress here that the fragmentation of organic compounds inside the Vocus may bias the  $C_{sat}$  results towards higher volatilities. 370 IVOC, which include generally less oxygenated VOCs, comprised the largest significant fraction of total organics (Vocus:  $49.945.8 \pm 5.45.8$  %; MION-Br:  $53.665.8 \pm 6.68.5$  %; MION-NO<sub>3</sub>:  $42.856.3 \pm 7.410.6$  %), indicating substantial oxidation extent of the precursor VOC, which made up  $48.753.7 \pm 5.56.1$  % of the total organics measured by Vocus but much less by MION-Br ( $\frac{8.510.4 \pm 8.18.2}{3.75.4 \pm 2.12.4}$  %; see Fig. 6b-d and Table 2). SVOC, which include slightly more oxygenated VOCs, constituted substantially 375 (Vocus:  $\frac{1.30.4}{1.30.4} \pm \frac{0.20.4}{0.20.4}$  %; MION-Br:  $\frac{24.316.2}{24.316.2} \pm \frac{34}{2.9}$  %; MION-NO<sub>3</sub>:  $\frac{27.523.9}{27.523.9} \pm \frac{3.25.1}{0.20.4}$  %) to the measured organic compounds. LVOC and ELVOC, which include OVOCs with higher oxidation degrees and mainly contribute to the growth of embryonic clusters in the atmosphere (Donahue et al., 2012;Bianchi et al., 2019), accounted for >14-8 % of the corresponding total organics measured by MION-Br and MION-NO<sub>3</sub>; while ULVOC, which include OVOCs with even higher oxidation extent that are the most effective drivers of pure biogenic 380 nucleation (Schervish and Donahue, 2020;Simon et al., 2020), accounted for  $\frac{0.70.5 \pm 0.6}{0.5 \pm 0.6}$  % of total organics measured by MION-NO<sub>3</sub> (see Fig. 6b-d and Table 2). Differences in the contribution of these compound groups (Fig. 6b-d and Table 2) could be due to different sensitivities of the instruments towards organic compounds with varying oxidation extent (Riva et al., 2019).

With the complementary molecular information of organic compounds from Vocus, MION-Br, and MION-385 NO<sub>3</sub>, a combined <del>VBS volatility distribution</del> 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 log10Csat value representing the bulk of all measured gaseous organic 390 compounds in this boreal forest was ~6.1  $\mu$ g m<sup>-3</sup>. In general, MION-NO<sub>3</sub> measured >96-91% of the ULVOC while MION-Br measured >51-70% of the ELVOC, and Vocus >84-98% of the SVOC, IVOC, and VOC (Figure \$88510). As we can see from Fig. 7b, organic compounds with  $C_{\text{sat}}$  of 10<sup>6</sup> µg m<sup>-3</sup> accounted for the biggest contributions. The VOC class was found to be the most abundant (about 49.4-53.2%), followed by the IVOC (about 48.945.9%), indicating that the bulk gaseous organic compounds observed in this boreal forest were relatively fresh, which is 395 also consistent with the bulk molecular composition's relatively low oxidation extent. Differences of the bulk volatility of organic compounds between daytime (between 10:00 and 17:00) and nighttime (between 22:00 and 05:00) were not significant (Figure <u>\$9\$11</u>). Given the location of the measurement station that is inside a borealforested area, the gaseous organic compounds were expected to be dominated by VOC and IVOC. The abundance of the CH compounds such as terpenes (see Table 1, Table <u>\$1\$2</u>, Fig. <u>\$3\$4</u>, and Fig. <u>\$5\$6</u>) as well as less 400 oxygenated VOC (see Fig. 3 and Fig. <u>\$4\$5</u>) support this conclusion. Although the condensable vapors (LVOC, ELVOC, and ULVOC) only comprised about  $\frac{0.30.2}{9}$  % of the total gaseous organic compounds, they contribute significantly to forming new particles via nucleation and further particulate growth and mass via condensation in this boreal forest (Kulmala et al., 2013;Ehn et al., 2014;Mohr et al., 2019). The results from the combined VBS could provide a better basis to test and improve parameterizations for predicting organic compound evolutions in transport and climate models.

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#### **4** Conclusions

In this paper, with an aim of obtaining a complete picture from VOCs to HOMs, the molecular composition and volatility of gaseous organic compounds (both VOC and OVOC) were investigated with the deployment of a Vocus and a MION APiAPI-ToF during April–July 2019 at the SMEAR II station situated in a boreal forest in Hyytiälä, 410 southern Finland. Similar to previous laboratory results (Riva et al., 2019), highest elemental O:C ratios of organic compounds were observed by the MION-NO<sub>3</sub>  $(0.9 \pm 0.1)$ , followed by the MION-Br  $(0.8 \pm 0.1)$ , and lowest by the Vocus  $(0.2 \pm 0.1)$ . Different from the pattern observed by Vocus which were mostly dominated by compounds with the number of carbon atoms between 3 and 10 and the number of oxygen atoms between 1 and 3 (i.e., less oxygenated monomers), compounds with larger number of carbon atoms (i.e., >10) and oxygen atoms (i.e., >3) 415 were much better detected by MION-Br (particularly for larger less oxygenated monomers and dimers) and MION-NO<sub>3</sub> (particularly for HOM monomers and dimers). The average mass-weighted chemical composition representing the bulk of all measured gaseous organic compounds in this boreal forest was C<sub>6.0</sub>H<sub>8.7</sub>O<sub>1.2</sub>N<sub>0.12</sub> indicative of the short carbon backbone and relatively low oxidation extent. Besides, diurnal patterns of the

measured organic compounds were found to vary among different measurement techniques, even for compounds 420 with the same molecular formula. The results indicate contributions of different isomers detected by the different techniques and/or fragmentation products from different parent compounds inside the instruments (e.g., Heinritzi et al., 2016;Zhang et al., 2017).

From the more complete picture of the bulk volatility of all measured organic compounds in this boreal forest, the average mass-weighted log<sub>10</sub>C<sub>sat</sub> value representing the bulk of all measured gaseous organic compounds in 425 this boreal forest was ~6.1  $\mu$ g m<sup>-3</sup>. In addition, the VOC class was found to be the most abundant (about 49.4 53.2%), followed by the IVOC (about 48.945.9%), indicating that the bulk gaseous organic compounds were relatively fresh, consistent with the bulk molecular composition's relatively low oxidation extent. Although condensable organic compounds (LVOC, ELVOC, and ULVOC) only comprised about 0.30.2 % of the total gaseous organic compounds, they play an important role, forming new particles via nucleation and contributing to 430 particulate growth and mass via condensation in this boreal forest (Kulmala et al., 2013;Ehn et al., 2014;Mohr et al., 2019).

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The results show the full characterization of the gaseous organic compounds in the boreal forest, and the advantages of combining Vocus and MION APiAPI-ToF for measuring ambient gaseous organic compounds with different oxidation extent (from VOCs to HOMs). Our study provides a more comprehensive understanding of the molecular composition and volatility of atmospheric organic compounds, as well as new insights when interpreting ambient measurements or using them as input to test and improve parameterizations for predicting organic compound evolutions in transport and climate models.

#### Data availability

Data are available upon request to the corresponding authors.

#### 440 **Author contributions**

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WH analyzed the MION APiAPI-ToF data, produced all figures, and wrote and edited the paper; HL operated and calibrated Vocus, analysed the Vocus data, provided suggestions for the data analysis, interpretation and discussion, and edited the paper; NS operated and calibrated MION APiAPI-ToF, preprocessed the MION APiAPI-ToF data, and provided suggestions for the data analysis, interpretation, and discussion; LH performed ACSM measurements, analyzed the ACSM data, and provided suggestions for the data interpretation and discussion; YJT provided suggestions for the data interpretation and discussion; JM helped with the MION measurements and provided suggestions for the data interpretation and discussion; SJT helped with the Vocus measurements; NMD provided suggestions for the data interpretation and discussion; MK organized the campaign and provided suggestions for the data interpretation and discussion; FB organized the campaign, provided suggestions for the data analysis, interpretation, and discussion, and edited the paper. All authors contributed to

the final text.

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# **Competing interests**

The authors declare no conflict of interest.

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**Figure 1.** Overview of the time series from April 16 to July 26, 2019. (**a**) temperature and global radiation; (**b**) wind direction and wind speed; (**c**) mixing ratios of SO<sub>2</sub> and O<sub>3</sub>; (**d**) mixing ratios of NO and NO<sub>2</sub>; (**e**) total gaseous organics measured by MION-Br and MION-NO<sub>3</sub>; and (**f**) total gaseous organics measured by Vocus as well as total particulate organics measured by ACSM. The data gap between MION-Br and MION-NO<sub>3</sub> (e.g., around May 17) was due to that the MION API-ToF was only running with API mode and NO<sub>3</sub> mode because of a mass flow controller issue for Br mode at that time.

**Table 1.** Contribution (%, average  $\pm 1$  standard deviation) of different compound groups to total organics measuredby different measurement techniques.

Compound group	Vocus	MION-Br	MION-NO <sub>3</sub>
СН	<del>31.8<u>35.2</u> ± 15.<u>1</u><del>3</del> %</del>	-	-
СНО	4 <u>5.943.6</u> ± 9. <u>4</u> <del>5</del> %	75.4 ± 5.3 %	71.8 ± 7.9 %
CHON	8.5 <u>8.1</u> ± 2.7 %	24.1 ± 5.2 %	28.1 ± 7.9 %
others	<del>13.8<u>13.1</u> ± 3.9 %</del>	0.5 ± 0.6 %	0.1 ± 0.1 %





**Figure 2.** (a) Mass defect plots for organic compounds measured by Vocus, MION-Br, and MION-NO<sub>3</sub>; (b) mass defect plots for organic compounds (separated into CH, CHO, CHON, and others) measured by Vocus, MION-Br, and MION-NO<sub>3</sub>. Markers in (b) were all sized by the logarithm of their corresponding concentrations.



**Figure 3.** Contribution of measured CHOX compounds with different number of oxygen atoms to total CHOX compounds as a function of the number of carbon atoms for Vocus (upper panel), MION-Br (middle panel), and MION-NO<sub>3</sub> (bottom panel). Vocus panel has excluded CHX compounds (i.e., O<sub>0</sub> compounds).



**Figure 4.** The median diurnal patterns of the total CH compounds measured by Vocus (**a**), CHO (**b**), and CHON compounds (**c**) measured by Vocus, MION-Br, and MION-NO<sub>3</sub> during the whole measurement period. Signals were normalized to their maximum values.



**Figure 5.** The median diurnal patterns of  $C_7H_{10}O_4$  (a),  $C_8H_{12}O_4$  (b),  $C_{10}H_{15}NO_6$  (c), and  $C_{10}H_{15}NO_7$  (d) measured by Vocus, MION-Br, and MION-NO<sub>3</sub> during the whole measurement period. Signals were normalized to their maximum values.

**Table 2.** Contribution (%, average ± 1 standard deviation) of different compound groups to total organics measuredby different measurement techniques based on the parameterization bymodifiedLi et al. (2016) approach (Daumitet al., 2013;Isaacman-VanWertz and Aumont, 2020).

Compound group	Vocus	MION Br	MION NO <sub>3</sub>
<del>ULVOC</del>	4	$0.0 \pm 0.0$ %	$0.7 \pm 0.6$ %
ELVOC	4	<del>2.3 ± 1.9 %</del>	<del>2.3 ± 1.0 %</del>
LVOC	0.1 ± 0.0 %	<del>11.3 ± 3.6 %</del>	<del>23.0 ± 5.2 %</del>
<del>SVOC</del>	$\frac{1.3 \pm 0.4 \%}{1.3 \pm 0.4 \%}$	<u>24.3 ± 3.9 %</u>	$27.5 \pm 3.2$ %
IVOC	$49.9 \pm 5.8 \%$	<del>53.6 ± 6.6 %</del>	4 <del>2.8 ± 7.4 %</del>
VOC	4 <del>8.7 ± 6.1 %</del>	<del>8.5 ± 8.1 %</del>	$3.7 \pm 2.1$ %

Compound group	Vocus	<u>MION-Br</u>	MION-NO <sub>3</sub>
ULVOC	<u>/</u>	$\underline{0.02\pm0.04~\%}$	$0.5 \pm 0.6$ %
ELVOC	7	<u>2.0 ± 1.8 %</u>	<u>2.3 ± 1.7 %</u>
LVOC	$0.02 \pm 0.01$ %	<u>5.6 ± 2.9 %</u>	<u>11.6 ± 5.1 %</u>
SVOC	$0.4 \pm 0.2$ %	$16.2 \pm 4.9 \%$	$23.9 \pm 5.1$ %
IVOC	$45.8 \pm 5.4$ %	<u>65.8 ± 8.5 %</u>	<u>56.3 ± 10.6 %</u>
VOC	<u>53.7 ± 5.5 %</u>	<u>10.4 ± 8.2 %</u>	<u>5.4 ± 2.4 %</u>



**Figure 6.** (a) Volatility distribution for measured organic compounds parameterized with the approach of modified Li et al. (2016) approach (Daumit et al., 2013;Isaacman-VanWertz and Aumont, 2020); resulting pie charts for the contributions of VOC, IVOC, SVOC, LVOC, ELVOC, and ULVOC for Vocus (b), MION-Br (c), and MION-NO<sub>3</sub> (d). Contribution of LVOC for Vocus (0.02 ± 0.01 %) and ULVOC for MION-Br ( $0.024 \pm 0.04$  %) was-were not labeled in the pie chart.



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—for—measured organic compounds parameterized with the approach of Li et al. (2016); (bc) resulting pie chart for the contributions of VOC, IVOC, SVOC, LVOC, ELVOC, and ULVOC.



**Figure S1.** Overlaps of all organic compounds (**a**), CHO compounds (**b**), and CHON compounds (**c**) measured by Vocus, MION-Br, and MION-NO<sub>3</sub>.



**Figure S2.** 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.



Figure <u>S2S3</u>. Wind speeds and directions during the measurement period.

**Table S1.** Full list of relatively long-lived species excluded from Vocus data present in this study.

Detected ion	Potential name
<u>C<sub>2</sub>H<sub>7</sub>O+</u>	Ethanol
<u>C<sub>3</sub>H<sub>7</sub>O+</u>	Acetone
$\underline{C_2H_5O_2+}$	Acetic acid
$\underline{C_2H_5O_3+}$	<u>Glycolic acid</u>
$\underline{C_3H_9O_2+}$	Acetone with water cluster



Figure <u>\$3\$4</u>. Time series of terpenes (isoprene, monoterpenes, sesquiterpenes, and diterpenes), and all organic
compounds (for comparison, same as in Fig. 1f), and all organic compounds + relatively long-lived compounds measured by Vocus.



Figure <u>S4S5</u>. Distribution of CHO compounds (a) and CHON compounds (b) measured by Vocus, MION-Br, and
 MION-NO<sub>3</sub> as a function of number of oxygen atoms vs. number of carbon atoms. Markers were sized by the logarithm of their corresponding concentrations.



**Figure <u>S5S6</u>**. Contribution of organic compounds with different number of oxygen atoms to all organic compounds (including CHX compounds) as a function of the number of carbon atoms measured by Vocus.

Compound group	Vocus	MION-Br	MION-NO <sub>3</sub>
C <sub>x</sub> H/CH	<del>35.5<u>38.3</u> ± 1<u>2.5</u><del>1.3</del> %</del>	-	-
C <sub>x</sub> HO/CHO	<del>27.3<u>27.4</u> ± 3.2 %</del>	$20.0 \pm 4.4$ %	26.8 ± 5.7 %
C <sub>x</sub> HON/CHON	$16.2 \pm 2.3$ %	34.9 ± 4.2 %	38.6 ± 4.5 %

**Table <u>S1S2</u>**. Sum contribution (%, average  $\pm 1$  standard deviation) of C<sub>x</sub>H, C<sub>x</sub>HO, and C<sub>x</sub>HON groups (x = 5, 10, 15, and 20) to total CH, CHO and CHON compounds measured by different measurement techniques.



Figure <u>S6S7</u>. The median diurnal patterns of temperature (a), global radiation (b), mixing ratios of SO<sub>2</sub> (c), O<sub>3</sub>
 (d), NO (e), and NO<sub>2</sub> (f) during the measurement period.





**Table S3.** Pearson's R correlations for dominant CHO and CHON species among different measurement techniques.

Compound	Vocus vs. MION-Br	Vocus vs. MION-NO <sub>3</sub>	MION-Br vs. MION-NO <sub>3</sub>
$\underline{C_7H_{10}O_4}$	<u>0.63</u>	<u>0.65</u>	<u>0.96</u>
$\underline{C_8}\underline{H_{12}}\underline{O_4}$	<u>0.64</u>	<u>0.66</u>	<u>0.96</u>
$\underline{C_{10}H_{15}NO_6}$	<u>0.35</u>	<u>0.36</u>	<u>0.93</u>
$\underline{C}_{10}\underline{H}_{15}\underline{NO}_{7}$	0.47	<u>0.43</u>	<u>0.94</u>


**Figure** <u>8759</u>**.** Comparison of the daytime (between 10:00 and 17:00) and nighttime (between 22:00 and 05:00) levels of  $C_x$ HO (**a**) and  $C_x$ HON (**b**) compounds (x = 5, 10, 15, 20) as a function of the number of oxygen atoms measured by Vocus (in pluses), MION-Br (in circles), and MION-NO<sub>3</sub> (in crosses). Compounds with higher signals during the daytime are colored in red and those with higher signals during the nighttime are colored in blue.



**Figure S8**<u>S10</u>**.** Fraction of ULVOC (a), ELVOC (b), LVOC (c), SVOC (d), IVOC (e), and VOC (f) detected by Vocus, MION-Br, and MION-NO<sub>3</sub>.



**Figure S9<u>S11</u>.** Stacked bar plots of combined volatility distribution for measured organic compounds parameterized with the <u>approach of modified</u> Li et al. (2016) <u>approach (Daumit et al., 2013;Isaacman-VanWertz</u>

and Aumont, 2020) during the daytime (a) and nighttime (c); resulting pie charts for the contributions of VOC, IVOC, SVOC, LVOC, ELVOC, and ULVOC during the daytime (b) and nighttime (d).

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