

Response to Referee Comment 1 (RC1)

The paper describes the results of organic trace gas measurements by Vocus PTRTOF in the French Landes forest in the summer of 2018. The Vocus PTR-TOF is a newly developed PTR-MS instrument with improved detection limits and mass resolution, and the paper highlights the large number of compounds that can be detected with this instrument. In addition to the more commonly measured monoterpenes, the paper presents measurements of sesquiterpenes and diterpenes. The paper also illustrates that many oxidation products of these hydrocarbon precursors are detected. The analysis of the data is rather descriptive and focuses on diurnal variations and the potential importance of different oxidants in forming the observed products. Overall, the paper is suitable for publication in Atmospheric Chemistry and Physics after incorporation of the comments below.

We thank the reviewer for the evaluation of the manuscript and the positive feedback. In the following, we answer the comments point by point and mention the changes that we made to our manuscript to address the reviewer's concerns and remarks.

Section 2: A better description of the site is needed. Specifically, VOCs are sampled at 2 m height, which is well inside the canopy. How high are the treetops in this forest and how open is the canopy? Several studies have shown how strongly the mixing ratios of monoterpenes, light-dependent VOCs like MBO and their oxidation products can depend on height within the canopy (Holzinger et al., 2005). Some more discussion of the results in this context would be good to add to the paper.

A more detailed description of the site has been added to the Section 2.1.

“Both population density and industrial emissions are low in this area. Due to the proximity of the Atlantic Ocean, the site has a strong maritime influence. The forest is largely composed of maritime pines (*Pinus pinaster* Aiton) and has an average height of ~10 m. Monoterpenes are known to be strongly emitted in the forest (Simon et al., 1994), which provides a good place for BVOCs characterization. A more detailed description of the site has been provided in earlier studies (Moreaux et al., 2011; Kammer et al., 2018; Bsaibes et al., 2019).”

Lines 38-40: The atmospheric chemistry of BVOCs has been studied much longer than just the past few years (Kanakidou et al., 2005). In general, the paper could do a better job citing the relevant literature. Much was learned about isoprene and monoterpene chemistry before the recent introduction of TOF-CIMS instruments.

We agree with the reviewer. More related literatures studying the atmospheric chemistry of BVOCs were added. “Over the past decades, a considerable amount of studies has been conducted to investigate the atmospheric chemistry of BVOCs (Kanakidou et al., 2005; Henze et al., 2006; Hatfield et al., 2011; Calfapietra et al., 2013; Jokinen et al., 2015; Ng et al., 2017).”

Line 49: “irreversibly” instead of “irremediably”.

Changed.

Lines 54-56: The lack of sesquiterpene measurements by PTR-MS are mostly due to a lack of sensitivity.

It has been changed to “due to the relatively low sensitivity”.

Lack 60-62: I recommend adding a quantitative indication rather than “drastically enhanced” to describe how the sensitivities compare with other instruments.

A quantitative description was added based on results from Holzinger et al. (2019). It has been changed to “with the enhanced sensitivities by a factor of ~10”.

Lines 97-99: I recommend adding the exact operating pressure in the reactor instead of a range. The difference between 1.0 and 1.5 mbar corresponds to a very large difference in E/N and therefore cluster ion distributions, fragmentation, etc.

We agree with the reviewer. Generally, the Vocus ionization sources is operated at a low pressure. In this work, we operated it at a pressure of 1.5 mbar. The exact description has been added.

Line 106: Have you considered how the use of nitrogen instead of zero air affects the ion chemistry and therefore background ion signals in the instrument?

Zero air was not available at the field site so we used pure nitrogen which was also needed for other collocated measurements. As shown below (Fig. 1), the mass spectra remain quite similar between zero measurements using pure nitrogen and ambient measurements.

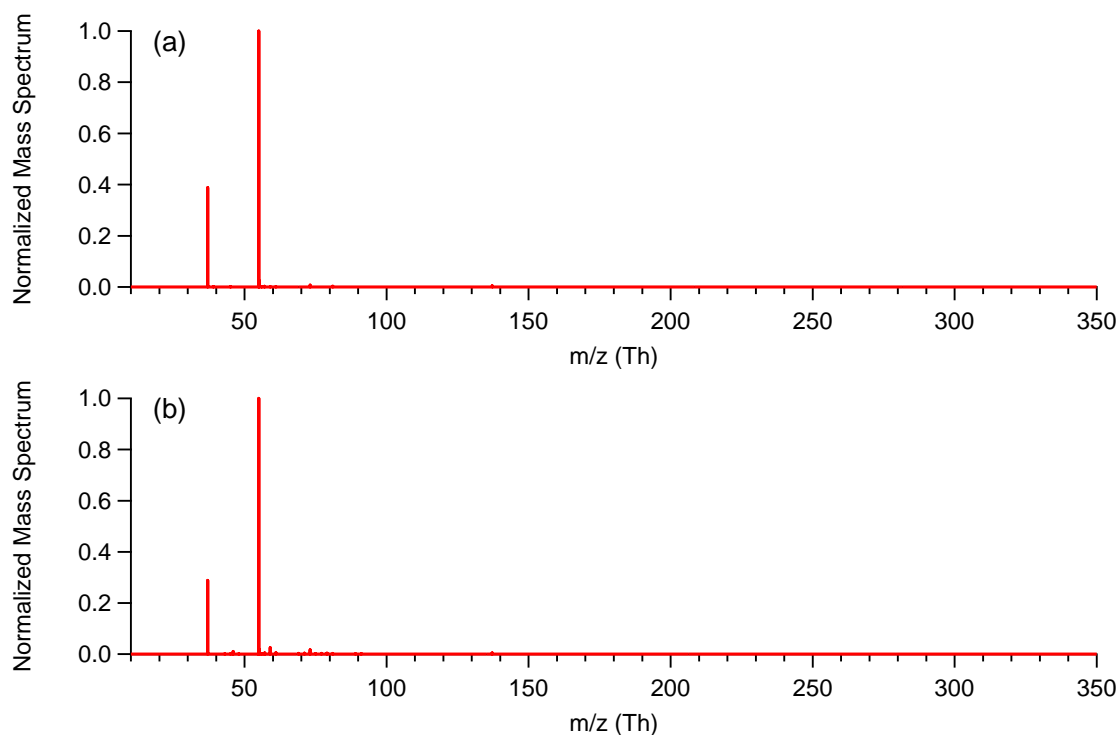


Figure 1. Example mass spectrum during (a) zero measurements using pure nitrogen and (b) ambient measurements.

Lines 117-118: This was not quite clear. Did your calibration mixture contain all three monoterpenes at 70 ppbv? In that case, your measured sensitivity is an average for the three monoterpenes. It is also not clear how you can use this average to determine the sensitivity as a function of reaction rate coefficient.

As described in the manuscript, the calibration mixture contains m/z 137 (alpha/beta pinene + limonene) and m/z 135 (*p*-cymene). For monoterpenes, yes, the measured sensitivity is an average for all these three monoterpenes. With the calculated sensitivities of monoterpenes and *p*-cymene and their rate constants, we built a linear regression of the sensitivity as a function of reaction rate coefficient.

Lines 117-118: The lack of calibration for an oxygenated compound is a concern. The distribution of H₃O⁺ and H₃O⁺(H₂O) reagent ions affects the sensitivity for hydrocarbons and polar molecules differently, but the distribution is difficult to determine in a Vocus PTR-TOF as H₃O⁺ ions are very poorly detected. As the exact quantification of oxidation products is not a major focus in this study, I do not think it is a problem, but moving forward the Authors should consider calibrating their instrument for a much wider range in compounds.

Thanks for the reviewer's suggestion. As the reviewer mentioned, the distribution of reagent ions affects the sensitivity of hydrocarbons and polar molecules differently. In the future, we consider calibrating the Vocus PTR-TOF with more oxygenated compounds, e.g., linanool oxide (C₁₀H₁₈O₂) and myrtenal (C₁₀H₁₄O).

Lines 120-122: I think this relationship needs to be included graphically. It seems that the range in rate coefficients is small and the resulting uncertainty in the factor 509.75 would consequently be very large.

As the reviewer suggested, the obtained empirical relationship has been included in the supplement as Figure S2. Due to the small difference between the rate coefficients of monoterpenes and *p*-cymene, we agree with the reviewer that the resulting uncertainty of the linear regression would be large. It has been noted in the revised manuscript: "Firstly, the small difference between the rate coefficients of monoterpenes and *p*-cymene may lead to large uncertainty in the established linear regression function between sensitivity and *k*. Calibrations with more VOC compounds should be performed in future works to cover a larger range of *k* values."

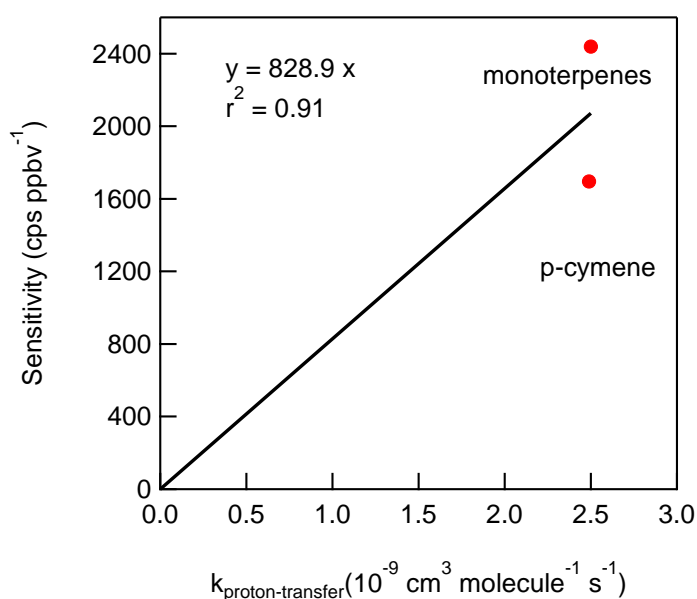


Figure S2. The built empirical relationship between the sensitivities and the proton-transfer reaction rate coefficients (*k*) using the calibrated data of monoterpenes and *p*-cymene: Sensitivity (cps ppbv⁻¹) = 828.9 × *k*.

Lines 123-125: It is trivial to determine the fragmentation of the monoterpenes in your calibration mixture and correct your measured sensitivities for fragmentation. This could be a large correction, so more detail needs to be given here.

The study by Sekimoto et al. (2017) demonstrated that the sensitivity of VOCs is linearly correlated with the proton transfer reaction rate constant k , considering the ion transmission efficiency and the fragmentation of protonated VOCs inside the PTR instruments. Within the Vocus PTR-TOF, Krechmer et al. (2018) have shown that the transmission efficiencies of ions $> m/z$ 100 Th reach up to 99%. Therefore, to calculate sensitivities using the method of Sekimoto et al. (2017), the fragmentation correction should be included in this study.

Previous studies have shown that within the PTR instruments, protonated monoterpenes mainly produce fragment ions at m/z 67, 81, and 95, and protonated *p*-cymene mainly produce fragment ions at m/z 41, 91, 93, and 119 (Tani et al., 2003). According to our terpene calibrations, the residual fraction of protonated monoterpenes and *p*-cymene after fragmentation in the Vocus PTR-TOF was on average 66% and 55%, respectively. Therefore, the measured sensitivities of monoterpenes and *p*-cymene were corrected for fragmentation to build the linear regression between sensitivity and k . The updated plot showing the corrected sensitivities as a function of k is displayed in Fig. S2. Detailed information has been added to the revised manuscript.

“Similar to conventional PTR instruments, the sensitivities of different VOCs in the Vocus PTR-TOF are linearly related to their proton-transfer reaction rate constants (k) when ion transmission efficiency and fragmentation ions are considered (Sekimoto et al., 2017; Krechmer et al., 2018). Krechmer et al. (2018) have shown that within the Vocus PTR-TOF, the transmission efficiencies of ions $> m/z$ 100 Th reach up to 99%. Therefore, the influence of fragmentation correction should be included in this study. According to terpene calibrations, the residual fraction was on average 66% and 55%, respectively, for protonated monoterpenes and *p*-cymene after their fragmentation within the instrument. Based on the corrected sensitivities for fragmentation and the k values of monoterpenes and *p*-cymene, an empirical relationship between the sensitivity and k was built from the scatterplots using linear regression: Sensitivity = $828.9 \times k$ (Fig. S2). Once k is available, the sensitivity of a compound can be predicted. Some studies found that isoprene may fragment significantly to m/z 41 (Keck et al., 2008; Schwarz et al., 2009). However, with the ambient data in this work, isoprene seems not to fragment much to $C_3H_5^+$, and they correlate poorly with each other (Fig. S3). Therefore, the fragmentation of isoprene is not considered for its quantification. Sesquiterpenes and some terpene oxidation products were found to fragment to varying degrees (Kim et al., 2009; Kari et al., 2018). Due to the lack of calibrations using other terpenes or terpene oxidation products, their fragmentation patterns within the Vocus PTR-TOF are not known in this work. Therefore, all the other terpenes and terpene oxidation products were quantified without consideration of fragment ions, which should be regarded as the lower limit of their ambient concentrations.”

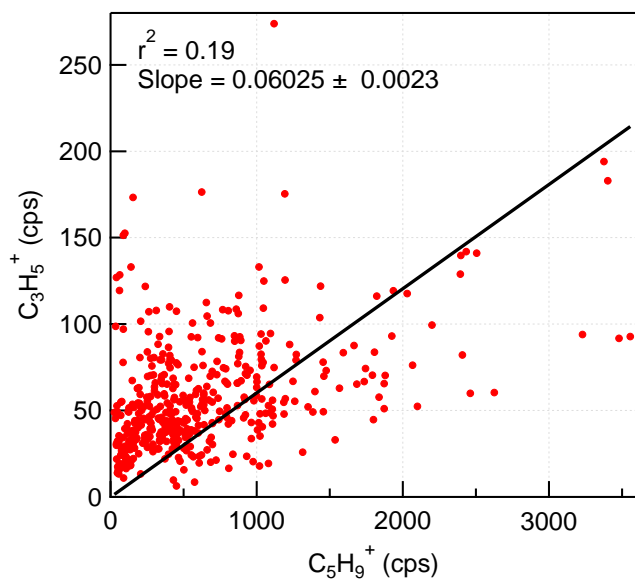


Figure S3. Correlation of the time variations between $C_3H_5^+$ and $C_5H_9^+$ signals.

Line 147: I do not think that inlet memory effects necessarily lead to an overestimate of sensitivities in this work. It all depends on how the passivation time of the inlet relates to the timescale of atmospheric variability. Memory effects can both lead to an underestimate and overestimate of measured mixing ratios.

Losses of gas-phase compounds or delays on their transfer happen when they go through Teflon tubing or chambers (Pagonis et al., 2017; Deming et al., 2019). Delays on the transfer of these compounds cause memory effects and can lead to underestimation or overestimation of their concentrations. However, the losses of some gas-phase compounds onto tubing surface or chamber wall, especially those low-volatility compounds, can be irreversible. Therefore, due to their worse transmissions compared to the more volatile compounds, their sensitivities may be overestimated and thus their concentration can be underestimated.

Lines 163-164: It would take a lot of monoterpenes to consume 50 ppbv of ozone. Some back of the envelope estimate may be useful to constrain the chemical sink of ozone. Surface uptake is likely another important sink of ozone in the canopy.

Due to the higher monoterpene concentrations in the Landes forest (up to ~40 ppb at night), the chemical sink of ozone may be higher. But we agree with the reviewer that, in addition to the gas phase reactions of O_3 with terpenes, plants can also act as a sink for ozone through direct uptake. The explanation has been added to the revised manuscript.

“In addition, plant surface uptake is likely another important ozone sink in the canopy (Goldstein et al., 2004).”

Lines 177-179: Use “exact mass” instead of “accurate mass”.

Changed.

Lines 187-187: C6-C9 hydrocarbons are also notable. Some of these can be fragments of monoterpenes and sesquiterpenes. Also, the mass cut-off by the BSQ affects what can be seen below m/z 40 and the readers need to be made aware of that.

The corresponding text has been modified in the revised manuscript.

“For hydrocarbons, multiple series with different carbon numbers were measured, especially those compounds containing 5 (“C₅”) to 10 carbon atoms (“C₁₀”), 15 carbon atoms (“C₁₅”), and 20 carbon atoms (“C₂₀”). Some of the C₅ – C₉ ions can be fragments of monoterpenes, sesquiterpenes, and their oxidation products (Tani et al., 2003, 2013; Kim et al., 2009; Kari et al., 2018). For ions < *m/z* 35 Th, the detection efficiency is considerably reduced due to the high-pass band filter of the BSQ (Krechmer et al., 2018).”

Lines 191-194: Biogenic butene is not very likely the cause for the elevated C₄H₉⁺ signal. As discussed, butanol is a more likely explanation. In addition, ions like C₃H₇⁺ and C₄H₉⁺ are very common fragments from many VOCs and are often prominent in the mass spectra (Pagonis et al., 2019).

Emissions of 1-butene have been measured in a midlatitude forest (Goldstein et al., 1996), a boreal wetland and forest floor (Hellén et al., 2006). Although in this study the biogenic butane does not likely explain the elevated C₄H₉⁺ signal as well as the corresponding time variations, the readers should be aware of potential biogenic contributions in the forest.

We agree with the reviewer that C₄H₉⁺ ions are very common fragment of many VOCs in PTR instruments and the corresponding explanation has been added to the revised manuscript.

“In addition, C₄H₉⁺ ions are very common fragments of many VOCs in PTR instruments and the peaks are prominent in the mass spectra (Pagonis et al., 2019).”

Lines 215-216: Add the difference between UTC and local time. Given the diurnal variations in Fig. 4, the definition of day- and nighttime data seems a bit off.

The difference between UTC and local time is two hours, which has been added in the revised manuscript (Local time = UTC time + 2). The daytime and nighttime are defined based on the availability of sunlight. As shown in Fig. 1, we can check from the diurnal variations of solar radiation.

Lines 224-235: I think the attribution of C₅H₉⁺ ions to isoprene should be considered in more detail. Isoprene mixing ratios are not very high in this study, and other VOCs are also detected at this mass. Notably, do the tree species at this site release MBO (Holzinger et al., 2005)?

In the PTR instruments, the detected C₅H₉⁺ ions can not only be isoprene but also fragments from many other compounds, i.e., cycloalkane and as mentioned by the reviewer 2-methyl-3-buten-2-ol (MBO). MBO undergoes collisional dissociation in the PTR and leads to the dominant fragment ion C₅H₉⁺ (Karl et al., 2012). It has been shown that 71% of the parent ion of MBO fragments into C₅H₉⁺ with an E/N ratio of 106 Td in a PTR-QMS (Warneke et al., 2003). At our measurement site, MBO was also detected by the Vocus PTR-TOF. However, due to the lack of MBO standards, we are not able to determine the fragmentation pattern of MBO within our instrument. As shown in the following figure, the C₅H₉⁺ signal is around 10 times higher than C₅H₁₁O⁺ signal. If C₅H₁₁O⁺ ions largely contributed to C₅H₉⁺, the correlation between these two ions is expected to be very good. However, as shown below, the correlation is weak (i.e., $r^2 = 0.33$). In addition, the diurnal variation of isoprene in Fig. 4a differs a lot with that of C₅H₁₁O⁺ in Fig. S7. All this information demonstrates that the fragmentation of MBO does not have a significant influence on the attribution of C₅H₉⁺ ions to isoprene in this study.

To make the readers aware of this, additional information has been added to the revised manuscript. “It has been shown that the attribution of $C_5H_9^+$ ions to isoprene with PTR instruments can be influenced by the fragmentation of many other compounds, i.e., cycloalkane and 2-methyl-3-buten-2-ol (MBO) (Karl et al., 2012; Gueneron et al., 2015). For example, using an E/N ratio of 106 Td in the PTR-MS with a quadrupole mass analyzer, 71% of the parent MBO fragmented to $C_5H_9^+$ ions (Warneke et al., 2003). However, in this study, the $C_5H_9^+$ signal was around 10 times as high as the $C_5H_{11}O^+$ signal and both ions correlated poorly with each other (Fig. S4; $r^2 = 0.33$). This information demonstrate that the fragmentation of MBO does not likely have a significant influence on the attribution of $C_5H_9^+$ ions to isoprene in this work.”

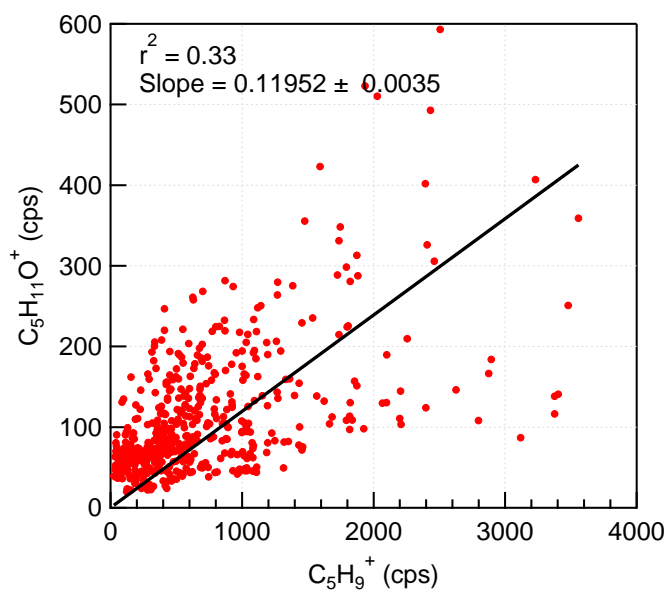


Figure S4. Correlation of the time variations between $C_5H_{11}O^+$ and $C_5H_9^+$ signals.

Lines 268-274: Some further explanation of how the authors think monoterpenes could be detected as C15 and C20 is needed here.

A previous study shows that during pure isoprene oxidation experiments, ion signals at $m/z = 137.133$ ($C_{10}H_{17}^+$) and $m/z = 81.070$ ($C_6H_9^+$) were detected by a PTR instrument (Bernhammer et al., 2018). These ion signals correspond to protonated monoterpenes and their major fragment. In this earlier study, two formation pathways of these signals were identified: secondary association reactions of protonated isoprene with isoprene within the PTR reaction chamber, and dimerization of pure isoprene inside the gas bottle to form monoterpenes. Similarly, in our ambient measurements, the detected C15 and C20 terpenes can possibly arise from the secondary association reactions of protonated monoterpenes with isoprene or monoterpenes respectively.

The corresponding explanation has been added in the revised manuscript.

“Bernhammer et al. (2018) have shown that secondary association reactions of protonated isoprene with isoprene can form monoterpenes within the PTR reaction chamber.”

Lines 290-292: The instrument settings used can indeed be the main explanation here and should be included in this paper.

Different instrument settings, especially the varying E/N ratios, can cause different fragmentation patterns of monoterpenes. As the E/N value decreases, the percentage of fragment ions decreases

because of the softer collisional reactions between H_3O^+ and monoterpene. However, in our ambient and chamber studies, the E/N values of Vocus PTR-TOF were quite similar, 118 Td and 120 Td, respectively. To make it clear, we added the E/N values for ambient and chamber studies in the revised manuscript.

“In our ambient and chamber studies, the E/N values of the Vocus PTR-TOF are quite similar, 118 Td and 120 Td, respectively.”

Lines 315-317: Methyl vinyl ketone and methacrolein are the most common products from isoprene reactions with OH. The observation of C4 products does not necessarily imply ozone reactions.

We agree with the reviewer that isoprene ozonolysis, where one carbon is always split off from the molecule, is not the only way to form C4 products. However, considering the peak concentration of isoprene and also the high ozone concentration at 8 pm in this study, isoprene ozonolysis is likely contributing to the formation of C4 products in addition to isoprene reactions with OH. Additional information of isoprene reactions with OH to form MVK ($\text{C}_4\text{H}_6\text{O}$) and MACR ($\text{C}_4\text{H}_6\text{O}$) has been included in the revised manuscript.

“Reaction with OH represents the largest loss pathway for isoprene in the atmosphere and produces a population of isoprene peroxy radicals (Wennberg et al., 2018). In the presence of NO, the major products are methyl vinyl ketone (MVK, $\text{C}_4\text{H}_6\text{O}$) and methacrolein (MACR, $\text{C}_4\text{H}_6\text{O}$).”

In addition, based on the competition between OH production and removal processes at night (Dusanter et al., 2008), the steady state OH concentration was estimated to be 0.012 ppt. With an O_3 concentration of ~20 ppb at 8 pm, the reaction rate of isoprene with OH radical was around 6 times as high as that of isoprene with O_3 . Details can be found in the following response.

Lines 327-337: This back-of-the-envelope analysis can be easily extended with estimates of the OH formation rate from alkene + ozone reactions, and the OH concentration in steady state. AN OH concentration of 10,000 seems very low.

If the competition between OH production and removal processes lead to a steady state of OH formation, an estimation of OH concentration can be calculated using the following equation (Dusanter et al., 2008):

$$[\text{OH}]_{SS} = \frac{k_{\text{O}_3+\text{VOC}}\alpha[\text{O}_3][\text{alkene}]}{k_{\text{OH}+\text{VOC}}[\text{alkene}] + k_{\text{OH}+\text{O}_3}[\text{O}_3]}$$

where $k_{\text{O}_3+\text{VOC}}$ is the rate constant for O_3 +alkene reaction with an OH yield of α , $k_{\text{OH}+\text{VOC}}$ is the rate constant for OH+alkene reaction, $k_{\text{OH}+\text{O}_3}$ is the rate constant for OH+ O_3 reaction. The rate constant of OH and O_3 reactions was obtained from Atkinson et al. (1992). At night, alkene concentrations in the Landes forest were dominated by monoterpenes, mainly α - and β -pinene (Riba et al., 1987; Simon et al., 1994). For the calculation of OH concentration, the loss of OH from reaction with O_3 was neglected, as it was much smaller than the loss of OH due to its reaction with monoterpenes (Gill and Hites, 2002). The rate constant of O_3 and monoterpene reactions was taken from Hakola et al. (2012), and the OH formation yield from O_3 and monoterpene reactions was obtained from Alicke et al. (2003). Finally, we assumed the equal contribution of α - and β -pinene to OH formation through alkene ozonolysis in this study. Hence, using an O_3 concentration of ~20 ppb at 8 pm, the OH concentration is estimated to be 0.012 ppt.

Details about the calculation of nighttime OH concentration from alkene ozonolysis have been added in the supplement. The corresponding text in the manuscript has been revised.

“Based on the competition between OH production and removal processes at night (Dusanter et al., 2008), the steady state OH concentration was estimated to be 0.012 ppt. Details can be found in the supplement. With an O₃ concentration of ~20 ppb at 8 pm, the reaction rate of isoprene with OH radical was around 6 times as high as that of isoprene with O₃.”

Figure 2: Some indication of the low mass cut-off is needed to fully appreciate this graph: the Vocus PTR-TOF is less sensitive below $m/z \sim 40$ depending on the BSQ settings and many readers will not fully understand that. The colors used in panel b for day and night are hard to distinguish for the color blind. In the caption, use “exact mass” instead of “accurate mass”.

It has been noted in the figure caption that ions $< m/z 35$ Th are detected at a much-reduced efficiency due to a high-pass band filter in the BSQ. The colors in Figure 2b have been updated to be color blind friendly. “Accurate mass” was changed to “exact mass”.

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Response to Referee Comment 2 (RC2)

Li et al. show novel and interesting results of time-resolved chemical composition at a forested field site in France with a focus on terpenoids. This is one of early practical deployments of the novel VOCUS instrument. The paper is well written and nicely explores the impressive analytical capability of the instrument in its detection of terpenes and their oxidation products although in some places the story line has a high potential for improvement in story coherence and connection to process understanding and other PTRMS studies. I would have a few relatively minor comments but overall, I do not see an issue with recommending this overall nice paper after addressing my comments.

We thank the reviewer for the evaluation of the manuscript and the positive feedback. In the following, we answer the comments point by point and mention the changes that we made to our manuscript to address the reviewer's concerns and remarks.

General

C1) It is clear from an impressively large number of VOC ions that what is discussed is only a portion of a complex VOC mixture in this ecosystem. These types of super novel contributions are needed to make a step-change in the progress in understanding the full picture of atmospheric chemistry and physics. The low detection limit allows for detection of a dramatically larger number of ions including highly reactive and difficult to measure sesquiterpenes and diterpenes which are just example classes. Therefore I am surprised why the authors did not go for the broader embracement of the chemical composition because terpenes and terpenoids are not all the chemical families emitted by the forest. It should be possible to pick up all mVOCs, less common terpenoids including C-methylated terpenes such as homoterpenes (e.g. C₁₁H₁₈, C₁₆H₂₆), benzenoids and secondary metabolites, well known in chemical ecology.

As shown in the manuscript, the Vocus PTR-TOF can detect large amounts of gas-phase signals in ambient deployment. It is difficult to characterize all the corresponding molecules within one publication. In addition, the main goal of this study is to demonstrate the capabilities of the recently developed Vocus PTR-TOF at measuring ambient air. To do this, terpenes were selected as the example because they are the main SOA precursor in the Landes forest, to propose a detailed analysis of their chemistry and highlight the performance of the Vocus PTR-TOF in characterizing atmospheric oxidation processes.

C2) I am curious about chlorine radical chemistry of the forest terpenoids and the capability of detection of these products by VOCUS. Recent studies suggest that chlorine radical is more extensive than previously thought including noncoastal areas and for many VOCs it is much faster than other radicals (Wang and Hildebrandt-Ruiz, 2017).

Theoretically, VOC compounds with higher proton affinity than H₃O⁺ can be detected by Vocus PTR-TOF. However, the chloride-containing compounds have not been successfully identified in this study. It is unknown if chloride-containing compounds are detected during our measurements. Peaks with unidentified chemical formula are named as "unknown" in the mass defect plot. However, it is worth pointing out that the oxidation of alpha-pinene by chlorine atoms seems to proceed mainly through the H-atom abstraction as recently shown by Wang et al. (2019).

Specific

C3) Abstract, L18, I was somewhat misled by elemental formula categories listed in the abstract. Are these really the only families detectable by VOCUS? What about halogenated, organometallic, and

metalloorganic ions? Do you disregard the order of the elements in the formula? For example, HCNO and HNCO are completely different molecules. This way of elemental categories makes it unclear how many of each element in a molecule can be detected. It might be less distracting to just mention what elements can be in a detectable molecule or create a master formula (e.g. C0-20H0- 42O0-9Si0-8: : :). What about inorganic compounds such as H₂S, ClNH₂?

There are probably additional compounds with other elemental compositions that can be detected by Vocus. But they cannot be assigned with a specific elemental composition and are thus listed as “others” in this work. The mass spectrometric technique of PTR instruments allows separation of isobaric ions but not isomers. Therefore, the order of the elements is generally disregarded. As mentioned in the abstract, CH, CHO, CHN, CHS, CHON, CHOS, and others are listed to show what kinds of elemental composition categories are detected by the Vocus at the site. The specific number of elements in each category will vary a lot depending on the environmental conditions of the measurements. Halogenated, organometallic, and metalloorganic ions are not successfully identified in this study. The PTR instruments have been used to measure H₂S in both laboratory and ambient environment. However, it was not detected in this work probably due to its very low concentration at this forest site. H₂S has very bad ion transmission in the Vocus. As mentioned above, chloride-containing compounds are not successfully identified in this study. With the reviewer’s suggestion, we checked the existence of ClNH₂ in the mass spectra and there seems to be a corresponding peak. But due to the interference of the high signals of H₃O⁺(H₂O)₂ (*m/z* 55 Th), the identification of ClNH₂ needs to be further evaluated.

C4) Abstract, L24, Why does the manuscript ignore an important Cl radical (e.g. Wang and Hildebrandt-Ruiz)?

The study by Wang and Hildebrandt-Ruiz (2017) investigated isoprene oxidation by Cl radicals. However, in this work, monoterpenes are the main SOA precursors in the Landes forest. As most of the oxidation products identified in this study do not contain any Cl, it is not possible to distinguish between Cl and OH-initiated oxidations. In addition, according to Wang et al. (2019), Cl-initiated oxidation of alpha-pinene does not produce much Cl-containing species.

C5) L30 what do you exactly mean by the relative term “ambient and remote”?

The ambient deployment of Vocus PTR-TOF was performed in a forested environment in this study, which is less influenced by anthropogenic sources. Hydrocarbon signals were dominated by monoterpenes. Therefore, the demonstrated capabilities of Vocus PTR-TOF were based on its performance in ambient and remote conditions in this work. The deployment of Vocus PTR-TOF in anthropogenic/polluted environment should be explored in future works.

C6) L31 Why did the authors focus so much on oxidation in this field site? There must be beautiful primary emissions so the general question is how can we understand the oxidation process without understanding the underlying process of recognizing the full range of primary compounds? It is not just terpenes that get oxidized.

A previous study by Kammer et al. (2018) suggests that terpene oxidations play an important role in SOA formation in the Landes forest. Therefore, the CERVOLAND campaign was organized to further assess the roles of BVOCs in aerosol formation at this forest site. During our measurements, monoterpene concentration reached up to 40 ppb at night and dominated the VOC emissions at this site. Therefore, terpene chemistry was investigated in this work as an example to achieve the goal.

C7) L43 What about all the other primary hemiterpenoids, homoterpenes (in particular DMNT, TMTT), meroterpenes, and terpenoids that will get oxidized?

The characteristics of some hemiterpenoids, i.e., prenil and isovaleric acid, have been illustrated in the manuscript and the supplement. For homoterpenes, DMNT was detected as a small peak during our measurements and TMTT was not clearly visible. The characteristics of some terpenoids, i.e., $C_{10}H_{16}O$ and $C_{10}H_{16}O_2$, were displayed in the manuscript and the supplement. However, it is true that not all BVOC compounds are investigated in this work. Since terpenes are characterized with much higher mixing ratios in the Landes forest, the oxidation processes of terpenes were demonstrated as the example to show the capabilities of the Vocus in atmospheric chemistry studies.

C8) L44 The formula of a diterpene is wrong here. Should be $C_{20}H_{32}$.

Corrected.

C9) L49 ULVOC is even less volatile than ELVOC (Schervish and Donahue, 2019).

Ultra-low volatility organic compounds (ULVOC) is a new class of organic products which is recently proposed by Schervish and Donahue et al. (2019). It has been added in the revised manuscript.

C10) L55-56 There are more PTRMS papers which reported SQT (e.g. Bourtsoukidis et al., 2018).

The ambient SQT measurements in Bourtsoukidis et al. (2018) were not performed with online PTR-MS but offline GC-MS.

C11) L99 The selection of the pressure range that is different from all the other CIMSeS is unclear. Did you lower the pressure because the sensitivity was saturatingly too high or because you could not otherwise reach the desired E/N? What was the E/N ratio? If you ran only at a single E/N ratio, did you make an effort to optimize it for minimizing fragmentation of monoterpenes?

As described by Krechmer et al. (2018), the Vocus PTR-TOF is not a CIMS.

Before the ambient measurements, the instrument was carefully tuned for the optimal performance and minimize fragmentation of product ions. The E/N ratio was 118 Td during the campaign.

C12) Monoterpenes and sesquiterpenes fragment slightly differently at different E/N ratios (Misztal et al., 2013; Kim et al., 2012). The issue is that except for long-lived sesquiterpenes such as cedrene or copaene (note that these were not evaluated by Kim et al., 2012) majority of sesquiterpenes will fragment on the monoterpene parent and fragment ions. A similar issue might be with fragmentation of diterpenes on sesquiterpene ions. Have you thought about an algorithm to subtract the fragment contribution from higher terpenes? Given that VOCUS seems uniquely skilled in higher terpene detectability, it could be a simple calibration measurement with LCU using most common isomers.

It is true that sesquiterpenes will fragment on monoterpene parent and fragment ions to varying degrees based on the study by Kim et al. (2009). However, no standard calibration was available for sesquiterpenes and diterpenes in this work. Therefore, the quantification of sesquiterpenes and diterpenes may be underestimated and that of monoterpenes may be overestimated. It has been noted in the revised manuscript so that the readers are aware of that.

“Kim et al. (2009) show that different sesquiterpenes fragment on monoterpene parent and fragment ions to varying degrees inside the PTR instruments. Without the consideration of sesquiterpene fragmentation, the quantification of sesquiterpenes in this work may be underestimated.”

In the future, the fragmentation of sesquiterpenes, diterpenes, and also some oxygenated compounds, inside the Vocus PTR-TOF should be investigated.

C13) L106 Did you use the completely dry N₂ for background measurements? Although the sensitivities are not affected by ambient humidity, I am not sure it has been shown how stable the backgrounds are at different humidities. It is known that the methanol chemical background in PTRMS strongly depends on the humidity so the humidity of zero air should be carefully investigated.

Unlike other PTRMS, it has been shown that the sensitivity of the Vocus is independent of the relative humidity which is explained by the high concentration of water within the ion molecule reactor (Krechmer et al., 2018). Therefore, we do not expect to have a noticeable impact of the RH when measuring the background of the instruments with the Vocus. Though change in RH can impact the partitioning of gaseous species within the sampling line which is not tested during the blank measurements (i.e., injection of the clean air directly in the front of the FIMR).

C14) L122 I do not have an issue with the simplified empirical approach to derive sensitivities from k 's as long as it is made clear that it is not generalizable to other conditions and instruments. In addition, I would expect the uncertainty is thoughtfully estimated and provided in the paper. However, this approach seems incorrectly applied to fragmenting compounds: "The predicted sensitivities with this method may be underestimated for compounds which do not fragment or fragment less than monoterpenes and cymene inside the PTR instruments." This does NOT make sense. One should sum up the known fragments and operate on the sum if the ions are pure and not interfering. It would be nice to see the monoterpene fragment distribution (e.g. Maleknia et al, 2007; Misztal et al., 2012) and if the sensitivity of the sum of fragments is consistent with the empirical k formula and explicit calibrations.

For both conventional PTR instrument and Vocus PTR-TOF, k and sensitivity are linearly correlated. But the established relationship in this study is not applicable to other conditions or instruments. we have made it clear in the manuscript.

Detailed procedure was provided to derive the linear regression function between k and sensitivities as well as potential uncertainty analysis. We agree with the reviewer that fragmentation of VOC compounds influence the derivation of the relationship. Therefore, as described in the response to referee #1, the fragmentation of monoterpenes and *p*-cymene inside the Vocus has been included. The influence of fragmentation on the quantification of other terpenes has also been discussed in the revised manuscript.

"Similar to conventional PTR instruments, the sensitivities of different VOCs in the Vocus PTR-TOF are linearly related to their proton-transfer reaction rate constants (k) when ion transmission efficiency and fragmentation ions are considered (Sekimoto et al., 2017; Krechmer et al., 2018). Krechmer et al. (2018) have shown that within the Vocus PTR-TOF, the transmission efficiencies of ions $> m/z$ 100 Th reach up to 99%. Therefore, the influence of fragmentation correction should be included in this study. According to terpene calibrations, the residual fraction was on average 66% and 55%, respectively, for protonated monoterpenes and *p*-cymene after their fragmentation within the instrument. Based on the corrected sensitivities for fragmentation and the k values of monoterpenes and *p*-cymene, an empirical relationship between the sensitivity and k was built from the scatterplots using linear regression: Sensitivity (cps ppb⁻¹) = 828.9 × k (Fig. S2). Once k is available, the sensitivity of a compound can be predicted. It should be noted that the established relationship in this study is not applicable to other conditions or instruments. Some studies found that isoprene may fragment

significantly to m/z 41 (Keck et al., 2008; Schwarz et al., 2009). However, with the ambient data in this work, isoprene seems not to fragment much to $C_3H_5^+$, and they correlate poorly with each other (Fig. S3). Therefore, the fragmentation of isoprene is not considered for its quantification. Sesquiterpenes and some terpene oxidation products were found to fragment to varying degrees (Kim et al., 2009; Kari et al., 2018). Due to the lack of calibrations using other terpenes or terpene oxidation products, their fragmentation patterns within the Vocus PTR-TOF are not known in this work. Therefore, all the other terpenes and terpene oxidation products were quantified without consideration of fragment ions, which should be regarded as the lower limit of their ambient concentrations.”

C15) L173. Could this result section title be rephrased to focus more on the science rather than the instrument?

The major aim of this study is to demonstrate the Vocus PTR-TOF capabilities and highlight the importance of its applications in atmospheric sciences. It is important that Section 3.2 focuses more on the instrument to show the strong capability of the Vocus PTR-TOF as this study is the first report on its ambient measurements. Therefore, we would like to keep the title of Section 3.2 as it is.

C16) L190-203. I must admit that I was a little surprised why the terpenoid-oriented paper suddenly jumps into discussing so vigorously the unrejected C4 fragment and the speculation to its multi-identity suddenly weakens the otherwise strong story. Undoubtedly, it could be butene and/or butanol fragment (confirmed by spikes from the use of butanol at the site), and/or trans-hexenal emitted from wounded plants. What was not discussed is that it could also be a product of residual O_2^+ chemistry of alkanes (e.g. Amador-Munos et al., 2017). This points me to the more important point that it is unclear if the impurity ions were controlled or even checked for their relative proportion to H_3O^+ ions? Apart from the $C_4H_9^+$ ion, one would also expect $C_3H_7^+$ and $C_5H_{11}^+$ ions from the O_2^+ chemistry. In any case, it is distracting to focus on the $C_4H_9^+$ ion so much in a terpenoid paper when you exclude from discussion hundreds of other probably more relevant and cleaner ions? I do not mean to criticize as it is overall a fair insight for the community but I would simply suggest moving this loose detail to SI to avoid unnecessary distraction.

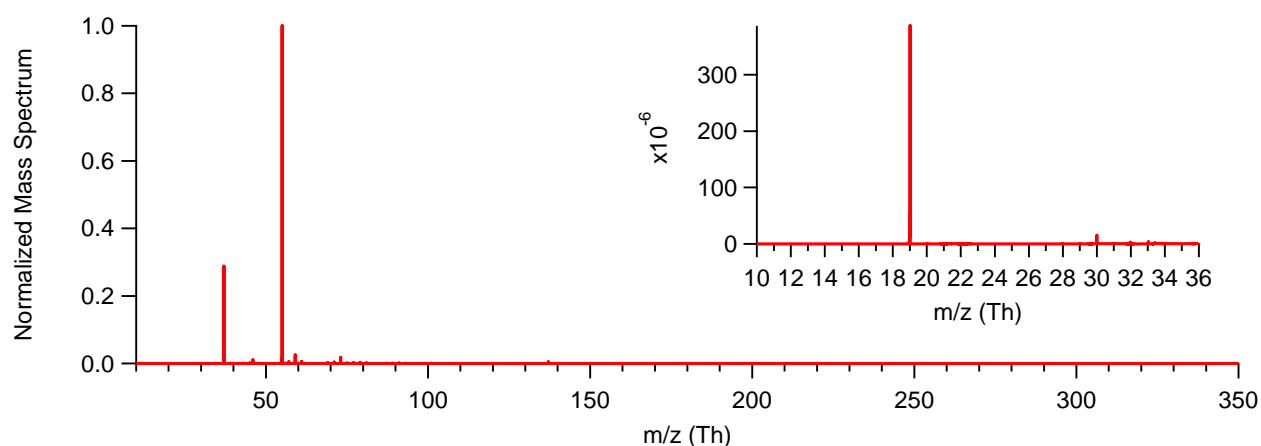


Figure 1. Example of the ambient mass spectra during the campaign, with a zoomed figure showing the relative proportion of O_2^+ and H_3O^+ ions.

For the impurity ions like O_2^+ and NO^+ , we checked their relative proportion to H_3O^+ ions in the mass spectra. Due to the high-pass band filter in the BSQ, O_2^+ , NO^+ , and H_3O^+ are all detected at a much-reduced efficiency by the Vocus PTR-TOF. As shown above, the signal intensity of H_3O^+ ions is much higher than that of O_2^+ and NO^+ during our campaign. Therefore, the influence of impurity ions

can be neglected in this study. The residual O_2^+ chemistry will not have a big contribution to the detected $C_4H_9^+$ ions.

Finally, it is important to mention that $C_4H_9^+$ ranked the third largest peak in hydrocarbon signals. Therefore, we believed that it is important to discuss the detection of such ion by Vocus. As the reviewer suggested, the related discussion has been moved to the supplement.

C17) L208-2013 Again, why suddenly mention volatile siloxanes in a forest? I found it super distracting. Of course, VOCUS can detect these compounds as was already shown in Riva et al., 2019. The paper could make a connection to an observation that these compounds are present even in forested air far from human contributions but the sudden shift to this group of compounds can confuse readers about the sources. If you really want to make a connection, why not to refer to an idea that the signal could be used to evaluate anthropogenic contributions at the site or find leaks in the system? Otherwise it makes sense to delete this distracting fragment or move it to SI.

As the reviewer suggested, discussions related to volatile siloxanes have been deleted to avoid unnecessary distraction.

C18) I like the beautiful figures in this ms showing off the amazing capability of VOCUS. However, the science emanating from them is simply asking to be discussed more than superficially. The local time (UTC+1) would be better for a reader to avoid additional mental processing. Figure 4 axes and labels are inconsistently bolded. Figure 2 shows many potentially super interesting halogenated ions which are completely ignored in grey.

This study is the first one that reports the ambient deployment of the recently developed Vocus PTR-TOF. Therefore, the major aim of this study, as mentioned above, is to demonstrate the capabilities of the Vocus PTR-TOF and highlight its importance in atmospheric science studies. But we agree that more scientific information from the data set needs to be explored deeply in the future.

During the CERVOLAND campaign, data are recorded in UTC time for both Vocus PTR-TOF and all the other collocated instruments. Therefore, the data are presented in UTC time for a better and convenient comparison among all the measurements.

Figure 4 has been updated for the inconsistency.

Data points shown in grey in Figure 2 indicate those unidentified peaks. In this study, the halogenated ions are not successfully identified.

C19) The authors are in a great position to make a further insight into processes. For example, a better connection could be made with boundary layer dynamics responsible for diel trends of light-dependent isoprene vs other terpenes which can be emitted and accumulated at night (e.g. might consult Kaser et al., 2013 for a PTRTOF comparison). In terms of oxidation insights there are many papers which could be consulted in terms of the products and mechanisms (e.g. Lee et al., 2006, Kurten et al., 2017) and make an even better and more coherent connection to these valuable initial VOCUS field measurements.

Consulting to Kaser et al. (2013) and other references related to terpene emissions, a better connection was made between diel trends of terpenes and boundary layer dynamics. The corresponding information has been added in the revised manuscript.

“Isoprene emissions are strongly light-dependent (Monson et al., 1989; Kaser et al., 2013).”

“Different from the light-dependence of isoprene emissions, monoterpene emissions are found to be mainly controlled by temperature (Hakola et al., 2006; Kaser et al., 2013). At night, monoterpenes can be continuously emitted and accumulated within the boundary layer. Therefore, monoterpenes showed the opposite diel pattern to isoprene and peaked during nighttime.”

We agree with the reviewer that the observations of terpenes and terpene oxidation products by Vocus PTR-TOF suggest complicated terpene chemical processes in the forest. However, as shown by Lee et al. (2006) and Kurten et al. (2017), laboratory simulations or theoretical computations are important to help figuring out the detailed chemical mechanisms. In addition to the Vocus ambient measurements, other data from collocated instruments, laboratory experiments, or theoretical simulations, are needed to provide a better figure of the complicated terpene chemical mechanisms, which is beyond the scope of this study. However, by evaluating the importance of different formation pathways in terpene chemistry in this study, we demonstrate the capability of the Vocus PTR-TOF at detecting a wide range of oxidized reaction products and highlight the importance of its application in atmospheric science studies.

Technical

C20) L61 “in” should be “of”

Changed.

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1 Terpenes and their oxidation products in the French Landes forest: 2 insight from Vocus PTR-TOF measurements

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12 **Abstract.** The capabilities of the recently developed Vocus proton-transfer-reaction time-of-flight mass spectrometer (PTR-
13 TOF) are reported for the first time based on ambient measurements. With the deployment of the Vocus PTR-TOF, we present
14 an overview of the observed gas-phase (oxygenated) molecules in the French Landes forest during summertime 2018 and gain
15 insights into the atmospheric oxidation of terpenes, which are emitted in large quantities in the atmosphere and play important
16 roles in secondary organic aerosol production. Due to the greatly improved detection efficiency compared to conventional
17 PTR instruments, the Vocus PTR-TOF identifies a large amount of gas-phase signals with elemental composition categories
18 including CH, CHO, CHN, CHS, CHON, CHOS, and others. Multiple hydrocarbons are detected, with carbon numbers up to
19 20. Particularly, we report the first direct observations of low-volatility diterpenes in the ambient air. The diurnal cycle of
20 diterpenes is similar to that of monoterpenes and sesquiterpenes, but contrary to that of isoprene. Various types of terpene
21 reaction products and intermediates are also characterized. Generally, the more oxidized products from terpene oxidations
22 show a broad peak in the day due to the strong photochemical effects, while the less oxygenated products peak in the early
23 morning and/or in the evening. To evaluate the importance of different formation pathways in terpene chemistry, the reaction
24 rates of terpenes with main oxidants (i.e., hydroxyl radical, OH; ozone, O₃; and nitrate radical, NO₃) are calculated. For the
25 less oxidized non-nitrate monoterpene oxidation products, their morning and evening peaks ~~likely~~ have contributions from
26 both O₃- and OH-initiated monoterpene oxidation. ~~Due to the decreased OH concentration at night, monoterpene ozonolysis~~
27 ~~becomes more important in the evening.~~ For the monoterpene-derived organic nitrates, oxidations by O₃, OH, and NO₃ radicals
28 all contribute to their formation, with their relative roles varying considerably over the course of the day. Through a detailed
29 analysis of terpene chemistry, this study demonstrates the capability of the Vocus PTR-TOF in the detection of a wide range
30 of oxidized reaction products in ambient and remote conditions, which highlights its importance in investigating atmospheric
31 oxidation processes.

32 1. Introduction

33 Organic aerosol (OA) constitutes a large fraction of atmospheric particles, having significant impacts on climate change, air
34 quality, and human health (Maria et al., 2004; IPCC, 2013; Mauderly and Chow, 2008). On a global scale, secondary OA
35 (SOA) is the largest source of OA, formed through the oxidation of volatile organic compounds (VOCs) (Jimenez et al., 2009).
36 Biogenic VOCs (BVOCs) are released into the atmosphere in high amounts, with an annual global budget being 760 Tg C
37 (Sindelarova et al., 2014). On average, SOA production from biogenic precursors ranges from 2.5 to 44.5 Tg C annually, which
38 is much larger than that from anthropogenic sources (Tsigaridis and Kanakidou, 2003). Over the past ~~few years~~ decades, a
39 considerable amount of studies has ~~ve~~ been conducted to investigate the atmospheric chemistry of BVOCs ([Kanakidou et al.](#),

40 [2005; Henze et al., 2006; Hatfield et al., 2011](#); Calfapietra et al., 2013; Jokinen et al., 2015; Ng et al., 2017). However, an
41 incomplete understanding of BVOCs characteristics and their oxidation processes in the atmosphere remains and yields large
42 uncertainties in quantitative estimates of air quality and climate effects of atmospheric aerosols (Carslaw et al., 2013; Zhu et
43 al., 2019).

44 Terpenes make up the main fraction of BVOCs (Guenther et al., 1995), encompassing isoprene (C_5H_8), monoterpenes
45 ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), diterpenes ($C_{20}H_{34}$) and even larger compounds. With one or more C=C double bonds in
46 their molecular structures, terpenes are highly reactive. After entering the atmosphere, terpenes can undergo oxidative
47 chemistry with the common atmospheric oxidants including hydroxyl radical (OH), ozone (O_3), and nitrate radical (NO_3).
48 These oxidation processes generate a large variety of organic species, with volatilities ranging from gas-phase volatile species
49 (VOC), to semi-volatile / low volatility organic compounds (SVOC and LVOC), to extremely low volatility organic
50 compounds (ELVOC) [and even ultra-low volatility organic compounds \(ULVOC\)](#), which [irreversibly irretrievably](#) contribute
51 to SOA formation (Donahue et al., 2012). Due to the chemical complexity and low concentrations of BVOCs oxidation
52 products, it remains extremely challenging to provide a comprehensive understanding of terpene chemistry in the atmosphere.

53 With a high time response and sensitivity, proton-transfer-reaction mass spectrometry (PTR-MS) has been widely
54 used to study the emissions and chemical evolution of VOCs in the atmosphere (Yuan et al., 2017). However, due to
55 [instrumental wall losses](#) [the relatively low sensitivity](#), previous PTR-MS instruments were not optimized to detect low volatility
56 compounds. For example, only a few ambient PTR-MS observations of sesquiterpenes are available (Kim et al., 2009; Jardine
57 et al., 2011). Correspondingly, it is not surprising that ambient observations of diterpenes, which are generally considered to
58 be non-volatile compounds, have never been reported. In addition, the existing PTR-MS is often not sensitive enough to
59 quantify terpene oxidation products at atmospherically relevant concentrations (Yuan et al., 2017). To address these
60 instrumental limitations, two new versions of PTR were recently developed, the PTR3 (Breitenlechner et al., 2017) and the
61 Vocus PTR-TOF (Krechmer et al., 2018), both coupled with a time of flight (TOF) mass analyzer. With the [drastically](#)
62 [enhanced sensitivities by a factor of ~10 \(Holzinger et al., 2019\)](#), these instruments are capable [of](#) detecting broader spectrum
63 of VOCs, where the detection of low-volatility VOCs is significantly improved compared to the conventional PTR-MS. Based
64 on the laboratory evaluation by Riva et al. (2019a), the Vocus PTR-TOF is able to measure both monoterpenes and lots of
65 monoterpene oxidation products containing up to 6 oxygen atoms.

66 Known for strong monoterpene emitters (Simon et al., 1994), the Landes forest in southwestern France is a suitable
67 place to investigate atmospheric terpene chemistry. A previous study at this site reported a high nocturnal monoterpene loading
68 and suggested that monoterpene oxidations play an important role in formation of new particles and the consequent growth of
69 atmospheric particles (Kammer et al., 2018). To better assess the roles of BVOCs in aerosol formation, the Characterization
70 of Emissions and Reactivity of Volatile Organic Compounds in the Landes Forest (CERVOLAND campaign) took place in
71 July 2018. The recently developed Vocus PTR-TOF was deployed in the CERVOLAND campaign to characterize terpenes
72 and their gas-phase oxidation products, which provides the first Vocus PTR-TOF measurement in a forested environment. In
73 this work, we present a comprehensive summary of the identified gas-phase molecules and gain insights into terpene chemistry
74 to demonstrate the Vocus PTR-TOF capabilities and the importance of its applications in atmospheric sciences.
75 Characterizations of isoprene, monoterpenes, sesquiterpenes, and particularly the rarely detected diterpenes, are reported. By
76 comparing the reaction rates of different formation pathways, we explore the formation mechanisms of terpene oxidation
77 products, including both non-nitrate and organic nitrate compounds.

78 2. Experimental methods

79 2.1 Measurement site

80 The Vocus PTR-TOF measurements were performed from 8 to 20 July, 2018 in the Landes forest (44°29'39.69"N,
81 0°57'21.75"W), as part of the CERVOLAND field campaign. The sampling site is situated at the European Integrated Carbon
82 Observation System (ICOS) station at Bilos in southwestern France along the Atlantic coast, ~40 km southwest from the
83 nearest urban area of the Bordeaux metropole. ~~Both population density and industrial emissions are low in this area. Due to~~
84 ~~the proximity of the Atlantic Ocean, the site has a strong maritime influence. A detailed description of the site has been given~~
85 ~~by Moreaux et al. (2011). Briefly, both population density and industrial emissions are low in this area.~~ The forest is largely
86 composed of maritime pines (*Pinus pinaster* Aiton) and has an average height of ~10m. ~~Monoterpenes are,~~ known ~~to be as a~~
87 ~~strongly emitted in the forest monoterpene emitter~~ (Simon et al., 1994), which provides a good place for BVOCs
88 characterization. ~~A more detailed description of the site has been provided in earlier studies (Moreaux et al., 2011; Kammer et~~
89 ~~al., 2018; Bsaibes et al., 2019).~~

90 2.2 Instrumentation

91 Compared to the conventional PTR instrument, the Vocus PTR-TOF used in this study is mainly differentiated in the following
92 aspects:

- 93 1. a new chemical ionization source with a low-pressure reagent-ion source and focusing ion-molecule reactor (FIMR),
- 94 2. no dependence of the sensitivity on ambient sample humidity due to the high water mixing ratio (10-20 % v/v) in the
95 FIMR,
- 96 3. employment of a TOF mass analyzer with a longer flight tube and faster sampling data acquisition card (mass
97 resolving power up to 15 000 m/dm),
- 98 4. an enhanced inlet and source design that minimizes contact between analyte molecules and inlet/source walls,
99 enabling detection of semi- and low-volatility compounds in a similar manner as chemical ionization mass
100 spectrometer (CIMS) instruments (Liu et al. 2019).

101

102 Details about the Vocus PTR-TOF are well described by Krechmer et al. (2018). Compared to the ionization in a conventional
103 PTR-MS at 2.0-4.0 mbar, a nitrate CIMS at ambient pressure, and an iodide CIMS at around 100 mbar, ~~we operate~~ the Vocus
104 ionization source ~~is generally operated~~ at a low pressure ~~(Krechmer et al., 2018) of 1.0-1.5 mbar. In this work, we operated the~~
105 ~~Vocus ionization source at a pressure of 1.5 mbar.~~ During the campaign, the Vocus PTR-TOF measurements were performed
106 at around 2 m above ground level (a.g.l), ~~thus within the canopy~~. Sample air was drawn in through 1-m long PTFE tubing (10
107 mm o.d., 8 mm i.d.) with a flow rate of 4.5 L min⁻¹, which helped to reduce inlet wall losses and sampling delay. Of the total
108 sample flow, only 150 sccm went into the Vocus, while the remainder was directed to the exhaust. The design of FIMR consists
109 of a glass tube with a resistive coating on the inside surface and four quadrupole rods mounted radially on the outside. With
110 an RF field, ions are collimated to the central axis, improving the detection efficiency of product ions. The mass resolving
111 power of the 1.2 m long TOF mass analyzer was 12 000-13 000 m/dm during the whole campaign. Data were recorded with a
112 time resolution of 5 s. Background measurements using high purity nitrogen (UHP N₂) were automatically performed every
113 hour.

114 The temperature, relative humidity (RH), wind speed, and ambient pressure were continuously monitored at 3.4 m
115 a.g.l. whereas the solar radiation was measured at 15.6 m a.g.l from a mast located at the site. The mixing ratios of nitrogen
116 oxides (NO_x) and ozone (O₃) were measured at 4 m a.g.l with UV absorption and chemiluminescence analyzers, respectively.
117 All data are reported in Coordinated Universal Time (UTC).

118 2.3 Data analysis and quantification of multiple compounds

119 Data analysis was performed using the software package “Tofware” (<https://www.tofwerk.com/software/tofware/>) that runs in
120 the Igor Pro environment (WaveMetrics, OR, USA). Tofware enables the time-dependent mass calibration, baseline
121 subtraction, and assignment of a molecular formula to the identified ions by high resolution analysis. Signals were averaged
122 over 30 min before mass calibration. Due to the high resolving power of the LTOF mass analyzer, isobaric ions were more
123 clearly separated. Examples of peak identification are given in Fig. S1.

124 The Vocus was calibrated twice a day during the campaign with a mixture (70 ppb each) of terpenes (m/z 137:
125 alpha/beta pinene + limonene; m/z 135: *p*-cymene) that was diluted using UHP N₂. Similar to conventional PTR instruments,
126 the sensitivities ~~for of~~ different VOCs in the Vocus PTR-TOF are linearly related to their ~~rate constants of the~~ proton-transfer
127 reactions rate constants (k) when ion transmission efficiency and fragmentation ions are considered (Cappellin et al.,
128 ~~2012~~ Sekimoto et al., 2017; Krechmer et al., 2018). Krechmer et al. (2018) have shown that within the Vocus PTR-TOF, the
129 transmission efficiencies of ions $> m/z$ 100 Th reach up to 99%. Therefore, the influence of fragmentation correction should
130 be included in this study. According to terpene calibrations, the residual fraction was on average 66% and 55%, respectively,
131 for protonated monoterpenes and *p*-cymene after their fragmentation within the instrument. Based on the corrected sensitivities
132 for fragmentation and the k values of monoterpenes and *p*-cymene, ~~Using the calculated sensitivities of monoterpenes and *p*-~~
133 cymene from calibration data and their respective rate constants (k), an empirical relationship between the sensitivity and k
134 was built from the scatterplots using linear regression: Sensitivity (cps ppb^{-1}) = ~~828.9509.75~~ $\times k$ (Fig. S2). Once k is available,
135 the sensitivity of a compound can be predicted. It should be noted that the established relationship in this study is not applicable
136 to other conditions or instruments. It should be noted that both monoterpenes and *p*-cymene fragment inside the instrument.
137 The predicted sensitivities with this method may be underestimated for compounds which do not fragment or fragment less
138 than monoterpenes and *p*-cymene inside the PTR instruments. Some studies found that isoprene may fragment significantly to
139 m/z 41 (Keck et al., 2008; Schwarz et al., 2009). However, with the ambient data in this work, isoprene seems not to fragment
140 much to C₃H₅⁺, and they correlate poorly with each other (Fig. S3). Therefore, the fragmentation of isoprene is not considered
141 for its quantification. Sesquiterpenes and some terpene oxidation products were found to fragment to varying degrees (Kim et
142 al., 2009; Kari et al., 2018). Due to the lack of calibrations using other terpenes or terpene oxidation products, their
143 fragmentation patterns within the Vocus PTR-TOF are not known in this work. Therefore, all the other terpenes and terpene
144 oxidation products were quantified without consideration of fragment ions, which should be regarded as the lower limit of
145 their ambient concentrations.

146 Rate constants for the proton-transfer reactions have only been measured for a subset of compounds. To quantify
147 terpenes and their oxidation products, we used the method proposed by Sekimoto et al. (2017) to calculate the rate constants
148 of different compounds with the polarizability and permanent dipole moment of the molecule. According to Sekimoto et al.
149 (2017), the polarizability and dipole moment of a molecule can be obtained based on the molecular mass, elemental
150 composition, and functionality of the compound. For a class of VOCs with the same number of electronegative atoms, their
151 polarizabilities can be well described using their molecular mass (Sekimoto et al., 2017). For VOCs containing a specific
152 functional group, it is found that their dipole moments are relatively constant based on results in the CRC Handbook (Lide,
153 2005). Since no isomer information is provided by mass spectrometry alone, it is challenging to figure out the functionality of
154 different compounds. Therefore, the polarizability and dipole moment of the compounds observed in this study were estimated
155 only based on the molecular mass and elemental composition. In this work, based on the physical properties of various
156 compounds in CRC Handbook (Lide, 2005) and the results in Sekimoto et al. (2017), we built the functions between
157 polarizability (α) and molecular mass (M_R) for different groups of VOCs and calculated the average dipole moment (μ) for
158 each group. For example, the polarizabilities of hydrocarbons were approximated as $\alpha = 0.142 M_R - 0.3$ and the dipole moment
159 was approximated to be zero. For the non-nitrate oxygenated compounds with one oxygen, $\alpha = 0.133 M_R - 1.2$, and the dipole
160 moment was averaged to be 1.6.

161 It should be noted that uncertainties are introduced to the calculated sensitivities in the following factors. Firstly, the
162 small difference between the rate coefficients of monoterpenes and *p*-cymene may lead to large uncertainty in the established
163 linear regression function between sensitivity and *k*. Calibrations with more VOC compounds should be performed in future
164 works to cover a larger range of *k* values. Secondly, as mentioned above, the theoretically calculated sensitivities of
165 sesquiterpenes, diterpenes, and terpene oxidation products, may be underestimated to varying extent without the consideration
166 of their fragment ions. oxidized compounds usually fragment more than terpene precursors in PTR instruments. For instance,
167 alcohol-containing compounds easily split off water and undergo the highest degree of fragmentation (Buhr et al., 2002). A
168 study by Kari et al. (2018) showed that around 95.5% of 1,8-cineole fragmented with an reduced electric field (*E*/*N*) of 130
169 Td. Molecules containing other functional groups fragment to varying, but lesser degrees; however, the theoretically calculated
170 sensitivities here should be regarded as upper limits for terpene oxidation products. Further, some low-volatility compounds
171 may experience wall losses inside the inlet tubing and the instrument and therefore have worse transmissions. The method in
172 this work may overestimate the sensitivities of these low-volatility compounds. In addition to proton transfer reactions, some
173 VOCs can be ionized through ligand switching reactions with water cluster ((H₂O)_nH₃O⁺) (Tani et al., 2004), thus increasing
174 their sensitivity. However, with the calibration standards used in this study, it is hard to estimate the effect of ligand switching
175 ionization. Lastly, uncertainties come from the estimation of polarizability and dipole moment of a molecule. With the method
176 used in this study, the sensitivity is calculated to be within 50% error when only the elemental composition of a compound is
177 known (Sekimoto et al., 2017).

178 3. Results and discussion

179 3.1 Meteorology and trace gases

180 Figure 1 displays the time variations of meteorological conditions and trace gases during the observation period. The weather
181 was mostly sunny, with solar radiation varying from 400 to 800 W/m² during daytime, indicating strong photochemical activity.
182 The ambient temperature and RH varied regularly every day. On average, the temperature was 22.8 ± 5.9 °C (mean ± SE),
183 ranging from 12.1 to 35.0 °C, which is favorable for BVOCs emissions in the forest. The average RH was 70.5 ± 19.0 % during
184 the campaign. Generally, the air masses were quite stable within the canopy. The wind speed never exceeded 1 m/s, indicating
185 the major influence of local sources on atmospheric processes in this study.

186 The O₃ levels fluctuated dramatically between day and night during the campaign. The average O₃ diurnal cycle
187 showed that O₃ concentration peaked up to ~50 ppb in the daytime. However, during most of the nights, O₃ concentration
188 dropped below 2 ppb. Considering the high nighttime concentration of terpenes observed by the previous study at this site in
189 the same season (Kammer et al., 2018), the low O₃ level at night suggests the large full consumption of O₃ by terpenes. Such
190 reactions of terpenes with O₃ can produce low volatility organic compounds, thus contributing to SOA formation (Presto et al.,
191 2005; Jokinen et al., 2014). In addition, plant surface uptake is likely another important ozone sink in the canopy (Goldstein
192 et al., 2004).

193 The NO concentration was generally low during the campaign, below detection limit (i.e., <0.5 ppb) most of the time.
194 However, clear NO plumes was sometimes observed in the early morning, as shown in Fig. 1e. The NO concentration peak at
195 4 am is probably the combination of local emission sources and low boundary layer. With the increasing sunlight afterwards,
196 the NO concentration started to decrease. A similar diel pattern of NO₂ was observed by the previous study at this site (Kammer
197 et al., 2018). The lower NO₂ concentration during daytime is likely explained by dilution with increasing boundary layer height
198 and NO₂ photolysis.

199 3.2 Vocus PTR-TOF capabilities in the forest

200 While Krechmer et al. (2018) and Riva et al. (2019a) have described the novel setup and performance of the Vocus PTR-TOF
201 and its application during a lab study, the instrument capability has not been fully explored in an ambient environment. Based
202 on the CERVOLAND deployment, we provide here, the first overview of gas-phase molecules measured by the Vocus PTR-
203 TOF in the forest. For a better visualization of the complex data set from real atmosphere, mass defect plots (averaged over
204 the whole campaign) are shown in Fig. 2 with the difference between the ~~exact~~ accurate mass and the nominal mass of a
205 compound plotted against its ~~exact~~ accurate mass. With the addition of hydrogen atoms, the mass defect increases, while the
206 addition of oxygen atoms decreases the mass defect. Therefore, changes in the mass defect plot help to provide information
207 on chemical transformation such as oxidation.

208 The mass defect plot in Fig. 2a is colored according to the retrieved elemental composition, with the black circle
209 indicating unidentified molecules. The size of the markers is proportional to the logarithm of the peak area of the molecule.
210 During the campaign, the Vocus PTR-TOF detected large amounts of (O)VOCs, with elemental composition categories of CH,
211 CHO, CHN, CHS, CHON, CHOS, and others. For hydrocarbons, multiple series with different carbon numbers were measured,
212 ~~especially those with~~ compounds containing 5 ~~carbon atoms~~ (“C₅”), to 10 carbon atoms (“C₁₀”), 15 carbon atoms (“C₁₅”), and
213 20 carbon atoms (“C₂₀”) ~~highlighted in the figure. Some of the C₅ – C₉ ions can be fragments of terpenes and their oxidation~~
214 ~~products (Tani et al., 2003, 2013; Kim et al., 2009; Kari et al., 2018). For ions <35 Th, the detection efficiency is much reduced~~
215 ~~due to a high-pass band filter of the BSQ (Krechmer et al., 2018).~~ Compared to the conventional PTR instruments, the
216 observation of larger hydrocarbon molecules by the Vocus PTR-TOF is mainly caused by the much lower wall losses and
217 increased detection efficiency. Hydrocarbon signals were largely contributed by monoterpene (C₁₀H₁₆H⁺) and its major
218 fragment (C₆H₈H⁺), indicating the monoterpene-dominated environment in the Landes forest (Kammer et al., 2018). According
219 to previous studies, monoterpene emissions in the Landes forest are dominated by α-pinene and β-pinene (Simon et al., 1994;
220 Kammer et al., 2018). The identified compound with the elemental composition of C₄H₉⁺ ranked the third largest peak in
221 hydrocarbons. ~~Detailed discussion about C₄H₉⁺ ions can be found in the supplement. One possible explanation for C₄H₉⁺ peak~~
222 ~~could be the protonated butene, which is emitted by vegetations or from anthropogenic sources (Goldstein et al., 1996; Zhu et~~
223 ~~al., 2017). The fragmentation of butanol also produces C₄H₉⁺ signals. Like many other alcohols, butanol can easily lose an OH~~
224 ~~during ionization in PTR sources (Spaniel and Smith, 1997). During the measurements at the Station for Measuring Ecosystem-~~
225 ~~Atmosphere Relations (SMEAR II) site in Hyytiälä Finland, Schallhart et al. (2018) concluded that C₄H₉⁺ signal detected by~~
226 ~~PTR TOF mainly came from butanol used by aerosol instruments, i.e., condensation particle counters (CPCs). In this study,~~
227 ~~CPCs using butanol to measure the particle concentration were also deployed at the site. While the exhaust air emitted from~~
228 ~~these collocated instruments was filtered using charcoal denuder, we cannot exclude the contribution of butanol to the~~
229 ~~identified C₄H₉⁺ signal. The spiky peaks in the time series of C₄H₉⁺ compound also indicated the influence of butanol (Fig.~~
230 ~~S2). Finally, the green leaf volatiles (GLV), a group of six-carbon aldehyde, alcohols and their esters which can be directly~~
231 ~~released by the plants, have been found to fragment at m/z 57 inside the PTR instruments (Rinne et al., 2005; Pang, 2015) and~~
232 ~~may also contribute to the observed C₄H₉⁺ signal.~~

233 In addition to the emitted precursors, the Vocus PTR-TOF detected various VOCs reaction products and
234 intermediates. Similar to the PTR3 measurements in the CLOUD chamber (Breitenlechner et al., 2017), many oxygenated
235 compounds from terpene reactions with varying degrees of oxidation were observed in this study. However, as a potential
236 limitation of the instrument, no dimers in the atmosphere were identified by the Vocus PTR-TOF, consistent with the results
237 from a previous laboratory deployment (Riva et al., 2019a). ~~Several cyclic volatile methyl siloxanes (VMS) were measured,~~
238 ~~which have been recently reported by conventional PTR TOF instruments (Yuan et al., 2017). Cyclic VMS are silicon-~~
239 ~~containing compounds widely used in cosmetics and personal care products (Buser et al., 2013; Yucuis et al., 2013). In this~~
240 ~~study, the identified peaks of cyclic VMS were protonated D3 siloxane (C₆H₁₈O₃Si₃), D4 siloxane (C₈H₂₄O₄Si₄), D5 siloxane~~

241 ~~(C₁₀H₂₀O₅Si₅), D6 siloxane (C₁₂H₃₆O₆Si₆), and their H₃O⁺ cluster ions. The existence of these peaks in the mass spectra helps~~
242 ~~to extend the range in mass or peak width calibrations.~~

243 Figure 2b compares the daytime and nighttime variations of different molecules, with the marker sized by the signal
244 difference between day and night. The daytime periods cover from 4:30 am to 7:30 pm, and the nighttime periods are from
245 7:30 pm to 4:30 am of the next day (both are UTC time; Local time = UTC time + 2). The data points are colored in orange
246 when the nighttime signal of the compound is larger than its daytime signal, and in green when the daytime signal is higher.
247 Patterns in the figure clearly show the difference in the diurnal variations of gas molecules with different oxidation degrees.
248 For example, most hydrocarbons are characterized with higher concentrations at night, which is largely caused by the stable
249 nocturnal boundary layer. The more oxidized compounds with more oxygen numbers are generally more abundant during the
250 day due to enhanced photochemistry, whereas the concentrations of the less oxidized compounds are mostly higher at night.
251 Details on the diurnal profiles of different oxidation products and their formation mechanisms are provided in Sect. 3.4.

252 3.3 Terpene characteristics

253 The characterizations of isoprene, monoterpenes, sesquiterpenes, and the rarely reported diterpenes, are investigated in this
254 study (Fig. 3, Fig. 4). On the global scale, isoprene is the most emitted BVOC species. It has been well established that
255 photooxidation of isoprene in the atmosphere contributes to SOA formation through the multiphase reactions of isoprene-
256 derived oxidation products (Claeys et al., 2004; Henze and Seinfeld, 2006; Surratt et al., 2010). However, recent advances on
257 isoprene chemistry found that isoprene can impact both particle number and mass of monoterpene-derived SOA by scavenging
258 hydroxyl and peroxy radicals (Kiendler-Scharr et al., 2009; Kanawade et al., 2011; McFiggans et al., 2019). During the
259 CERVOLAND campaign, the average mixing ratio of isoprene was 0.6 ppb, consistent with the mean value of 0.4 ppb reported
260 for the LANDEX campaign during summer 2017 at the same site (Mermet et al., 2019). These values are much lower than that
261 in the southeastern United States (Xiong et al., 2015) and Amazon rainforest (Wei et al., 2018) but higher than observations
262 in the boreal forest at the SMEAR II station (Hellán et al., 2018). Isoprene emissions ~~require sunlight~~ are strongly light-
263 dependent (Monson et al., 1989; Kaser et al., 2013). Therefore, a pronounced diurnal pattern of isoprene was observed with
264 maximum mixing ratios occurring during daytime and minima at night. It has been shown that the attribution of C₅H₉⁺ ions to
265 isoprene with PTR instruments can be influenced by the fragmentation of many other compounds, i.e., cycloalkane and 2-
266 methyl-3-buten-2-ol (MBO) (Karl et al., 2012; Gueneron et al., 2015). For example, using an E/N ratio of 106 Td in the PTR-
267 MS with a quadrupole mass analyzer, 71% of the parent MBO fragmented to C₅H₉⁺ ions (Warneke et al., 2003). However, in
268 this study, the C₅H₉⁺ signal was around 10 times as high as the C₅H₁₁O⁺ signal and both ions correlated poorly with each other
269 (Fig. S4; r² = 0.33). This information demonstrate that the fragmentation of MBO does not likely have a significant influence
270 on the attribution of C₅H₉⁺ ions to isoprene in this work.

271 As expected, monoterpenes showed the highest mixing ratios among all the terpenes, with an average value of 6.0
272 ppb. On July 9, a heavy monoterpene episode occurred at night, with the monoterpene mixing ratio reaching as high as 41.2
273 ppb. Comparatively, the average monoterpene level observed in this work is similar to the measurements performed in 2015
274 and 2017 at the same site (Kammer et al., 2018; Mermet et al., 2019) and more than ten times higher than that observed in the
275 boreal forest at SMEAR II in summer (Hakola et al., 2012; Hellán et al., 2018). The high concentration of monoterpenes
276 indicates the potential significance of monoterpene-related aerosol chemistry in the Landes forest. Different from the light-
277 dependence of isoprene emissions, monoterpene emissions are found to be mainly controlled by temperature (Hakola et al.,
278 2006; Kaser et al., 2013). At night, monoterpenes can be continuously emitted and accumulated within the boundary layer.
279 Therefore, monoterpenes showed the opposite diel pattern to isoprene and peaked during nighttime. Opposite to the diurnal
280 variations of isoprene, monoterpene concentrations peaked at night, caused by the stable nocturnal boundary layer. During
281 daytime, the concentration of monoterpenes dropped to around 0.9 ppb, due to the increased atmospheric mixing after sunrise
282 and the rapid photochemical consumptions.

283 A study in Hyytiälä concluded that sesquiterpenes, due to their higher reactivity, could play a more important role in
284 O₃ chemistry than monoterpenes, even though the concentration of sesquiterpenes was much lower (Hellén et al., 2018).
285 However, the short lifetimes of sesquiterpenes also mean that their concentrations will be highly dependent on the sampling
286 location at a given site. Some studies also proposed that sesquiterpene oxidation products are linked to atmospheric new particle
287 formation (Bonn and Moortgat, 2003; Boy et al., 2007). Despite the potential importance of sesquiterpenes in aerosol chemistry,
288 the available data on ambient sesquiterpene quantification remains still quite limited. In this work, the mixing ratios of
289 sesquiterpenes were found to vary from 8.9 ppt to 408.9 ppt in the Landes forest, with an average of 64.5 ppt during the
290 observations. This sesquiterpene level is comparable to that reported by Mermet et al. (2019) in summer 2017 at the same site
291 and observations by Jardine et al. (2011) in Amazonia but higher than previous measurements at SMEAR II station (Hellén et
292 al., 2018). Kim et al. (2009) show that different sesquiterpenes fragment on monoterpene parent and fragment ions to varying
293 degrees inside the PTR instruments. Without the consideration of sesquiterpene fragmentation, the quantification of
294 sesquiterpenes in this work may be underestimated. As shown in Fig. 4, sesquiterpenes displayed a similar diurnal pattern with
295 monoterpenes, consistent with observations in other areas (Jardine et al., 2011; Hellén et al., 2018).

296 While diterpenes are present in all plants in the form of phytol, they have been thought for a long time not to be
297 released by vegetation due to their low volatility (Keeling and Bohlmann, 2006). In 2004, von Schwartzberg et al. (2004)
298 reported for the first time the release of plant-derived diterpenes into the air. A recent study found that the emission rate of
299 diterpenes by Mediterranean vegetation was in the same order of magnitude as monoterpenes and sesquiterpenes (Yáñez-
300 Serrano et al., 2018). For the first time, this study reports the ambient concentration of diterpenes in a forest. According to the
301 Vocus PTR-TOF measurements, the average mixing ratio of diterpenes was around 2 ppt in the Landes forest. Considering the
302 low volatility of diterpenes and their potential wall losses inside the inlet tubing and the instrument, the diterpene concentration
303 might be higher. Similar to monoterpenes and sesquiterpenes, diterpenes presented peak concentrations at night and lower
304 levels during the day. Although the amounts of diterpenes in the atmosphere are hundreds to thousands times lower than those
305 of monoterpenes and sesquiterpenes, diterpenes potentially play a role in atmospheric chemistry due to their unsaturated
306 structure and high molecular weight (Matsunaga et al., 2012). Up to now, there is no report on the possible atmospheric
307 implications of diterpenes, which should deserve more attention in the future.

308 Considering the similar atmospheric behaviors of monoterpenes, sesquiterpenes, and diterpenes in this study, it is
309 questioned if the observed sesquiterpenes and diterpenes are real signals in the atmosphere or generated by monoterpenes in
310 the instrument. Bernhammer et al. (2018) have shown that secondary association reactions of protonated isoprene with isoprene
311 can form monoterpenes within the PTR reaction chamber. Figure 5 illustrates the scatter plots among monoterpenes,
312 sesquiterpenes, and diterpenes, colored by time of the day. At night, both sesquiterpenes and diterpenes correlated well with
313 monoterpenes. However, their correlation with monoterpenes got weaker during daytime as the data points became more
314 scattered. This suggests that the observations of sesquiterpenes and diterpenes are real emissions in the atmosphere.
315 Comparatively, sesquiterpenes and diterpenes showed a strong correlation with each other through the whole day ($r^2 = 0.85$).

316 **3.4 Insights into terpene chemistry**

317 **3.4.1 Comparison with chamber results**

318 Due to the diverse precursors and changing environmental conditions in the ambient air, it is challenging to retrieve all the
319 atmospheric chemical processes occurring within the Landes forest. To start with, we compare the ambient data with those
320 from α -pinene ozonolysis in the presence of NO_x conducted in the COALA chamber at the University of Helsinki. A detailed
321 description of the laboratory experiment is provided elsewhere (Riva et al., 2019a, 2019b). According to literature,
322 monoterpenes undergo some degree of fragmentation within the PTR instrument, producing dominant ions of C₆H₉⁺, C₃H₇⁺,
323 C₇H₁₁⁺, et al (Tani et al., 2003, 2013; Kari et al., 2018). As illustrated in Fig. 6, C₆H₉⁺ is the largest fragment produced by
324 monoterpenes within the Vocus PTR-TOF. However, a clear difference of monoterpene fragmentation pattern is observed in

325 the mass spectra of ambient observations and chamber experiments. While the signal of $C_6H_9^+$ is lower than that of $C_{10}H_{17}^+$
326 during the field deployment, $C_6H_9^+$ peak is higher than $C_{10}H_{17}^+$ peak in the chamber study. Based on the monoterpene
327 calibration data, the $C_6H_9^+$ signal is around 40% and 138% of the protonated monoterpene signal in ambient deployment and
328 chamber experiment, respectively. The larger presence of the $C_6H_9^+$ peak in the chamber study can be likely explained by the
329 much higher concentrations of oxygenated terpenoids during the chamber experiments. Indeed, previous studies have shown
330 that oxygenated terpenoids, including linalool and pinonaldehyde, fragment inside the PTR instrument and produce a dominant
331 ion at m/z 81 (Maleknia et al., 2007; Tani, 2013). Different settings of the instrument ~~in the two studies~~ can also contribute to
332 ~~the difference~~ different fragmentation patterns of monoterpenes (Tani et al., 2003, 2013; Kari et al., 2018). In our ambient and
333 chamber studies, the E/N values of the Vocus PTR-TOF are quite similar, 118 Td and 120 Td, respectively. In addition, the
334 fragmentation patterns vary among individual monoterpene species due to their different physicochemical properties (Tani et
335 al., 2013; Kari et al., 2018). Considering that α -pinene is the only monoterpene species injected in the chamber experiment,
336 the combination of various monoterpenes in the atmosphere likely introduces additional differences in the fragmentation
337 pattern.

338 Gas-phase ozonolysis of alkenes generates OH radicals in high yields (Rickard et al., 1999). Without an OH scavenger,
339 both O_3 - and OH-initiated oxidations happened during α -pinene ozonolysis in the chamber. Using the Vocus PTR-TOF,
340 various oxidation products were identified in the chamber study, with the dominant species being $C_7H_{10,12}O_{3-6}$, $C_8H_{14}O_{3-6}$,
341 $C_9H_{14}O_{1-5}$, and $C_{10}H_{14,16}O_{2-6}$. In comparison, more oxygenated compounds which were directly emitted or from monoterpene
342 reactions were observed in ambient air due to complex environmental conditions, with the oxygen number ranging from 1 to
343 7. Therefore, the Vocus PTR-TOF measurements provide the opportunity to characterize both the emitted precursors and the
344 resulting oxidation products. During the chamber experiments, NO_2 was injected and photolyzed using 400nm LED lights to
345 generate NO. In the presence of NO_x , organic nitrates were formed from the reactions between NO and monoterpene-derived
346 peroxy radicals (RO_2). The major organic nitrates observed were $C_9H_{13,15}NO_{6-8}$ and $C_{10}H_{13,15}NO_{3-8}$. Compared to the chamber
347 study, more organic nitrates of C_8 , C_9 , and C_{10} from monoterpene reactions were identified in CERVOLAND data. It is worth
348 pointing out that the combination of different monoterpene species in the ambient environment may result in various types of
349 organic nitrates through different formation pathways.

350 3.4.2 Non-nitrate terpene oxidation products

351 Based on the ambient observations, the non-nitrate oxidation products from isoprene, monoterpenes, and sesquiterpenes, are
352 investigated in this study. Isoprene gas-phase products are mainly represented by C_4 and C_5 compounds (Wennberg et al.,
353 2018). In this work, we consider $C_4H_{6,8}O_n$ and $C_5H_{8,10,12}O_n$ ($n=1\sim 6$) as the dominant non-nitrate products from isoprene
354 oxidations. The diurnal variations of $C_5H_8O_n$ are displayed in Fig. 7 and the others in Fig. ~~S53-75~~. Generally, all these oxidation
355 products displayed an evening peak at around 8 pm, which may come from the O_3 - or OH-initiated isoprene oxidations.
356 Reaction with OH represents the largest loss pathway for isoprene in the atmosphere and produces a population of isoprene
357 peroxyl radicals (Wennberg et al., 2018). In the presence of NO, the major products are methyl vinyl ketone (MVK, C_4H_6O)
358 and methacrolein (MACR, C_4H_6O). Globally, reactions with O_3 contribute a small fraction of approximately 10% to isoprene
359 removal in the atmosphere (Wennberg et al., 2018). When isoprene reacts with O_3 , one carbon is always split off from the
360 molecule (Criegee, 1975). Considering the peak concentration of isoprene at 8 pm and the relatively high O_3 concentration at
361 the moment (Figs. 1 and 4), isoprene ozonolysis is also likely contributing to the formation of C_4 oxidation products. Because
362 OH radicals can be efficiently produced from alkene ozonolysis (Pfeiffer et al., 2001), the OH-initiated oxidation of isoprene
363 can also be an important formation pathway of these oxidation products in the evening. For example, as a predominant product
364 from the reactions of isoprene with OH, $C_5H_{10}O_3$ (corresponding to isoprene hydroxy hydroperoxide and/or isoprene
365 epoxydiols) presented a clear single peak in the evening. To determine the relative importance of O_3 - and OH-initiated

oxidations in isoprene chemistry at night, the reaction rates (R) of isoprene with O₃ and OH radical were compared by Eq. (1) and Eq. (2):

$$R_{\text{ISO+OH}} = k_{\text{ISO+OH}}[\text{ISO}][\text{OH}] \quad (1)$$

$$R_{\text{ISO+O}_3} = k_{\text{ISO+O}_3}[\text{ISO}][\text{O}_3] \quad (2)$$

where k is the reaction rate coefficient of isoprene with OH or O₃, and [ISO], [OH] or [O₃] is the concentration of isoprene, OH radical or O₃.

Taking the evening peak of isoprene oxidation products at 8 pm as an example, we compared the roles of O₃ and OH radicals in their formation. Laboratory studies have shown that the reaction rate coefficient of isoprene with OH radical is generally 10⁷ times larger than that of isoprene with O₃ (Dreyfus et al., 2002; Kari et al., 2004). ~~Based on the competition between OH production and removal processes at night (Dusanter et al., 2008), the steady state OH concentration was estimated to be 0.012 ppt. Details can be found in the supplement. According to literature, the nighttime concentration of tropospheric OH radical varies in the range of $1 \times 10^4 - 1 \times 10^5$ molecule cm⁻³ (0.0004 - 0.004 ppt) in the field (Shirinzadeh et al., 1987; Khan et al., 2008; Petäjä et al., 2009; Stone et al., 2012). Therefore, with an O₃ concentration of ~20 ppb at 8 pm, if the OH concentration was around 1×10^4 molecule cm⁻³ (0.0004 ppt) at the moment, the reaction rate of isoprene with OH radical was around 0.26 times as high as that of isoprene with O₃. If the OH concentration reached up to 1×10^5 molecule cm⁻³ (0.004 ppt) at 8 pm, the reaction rate of isoprene with OH radical was 2 times higher than that of isoprene with O₃.~~ For the more oxidized compounds from isoprene oxidations, their concentrations had a broad daytime presence from 10 am to 8 pm due to strong photooxidation processes. Similar diurnal variations of C₄H_{6,8}O_{5,6} and C₅H_{8,10,12}O_{5,6} measured by nitrate CIMS have been observed in an isoprene-dominated environment at Centreville, Alabama (Massoli et al., 2018).

The diurnal patterns of C₈H_{12,14}O_n, C₉H₁₄O_n, and C₁₀H_{14,16,18}O_n (n=1~6) were illustrated to characterize monoterpene oxidations in the Landes forest (Fig. 8; Fig. S86-120). For the less oxidized compounds with oxygen numbers from 1 to 4, most of them were observed with clear morning and evening peaks, which can be produced from O₃- and OH-initiated monoterpene oxidations. For the morning peak at around 7 am, the relative roles of O₃- and OH-initiated monoterpene oxidation were evaluated using the similar method as in Eq. (1) and Eq. (2). The reaction rate coefficient of monoterpene + OH is approximately 10⁶ times higher than that of monoterpene + O₃ (Atkinson et al., 1990; Khamaganov and Hites, 2001; Gill and Hites, 2002; Hakola et al., 2012). In the morning, typical tropospheric OH concentrations have been observed to be around $1 \times 10^5 - 1 \times 10^6$ molecule cm⁻³ (0.004 - 0.04 ppt) (Shirinzadeh et al., 1987; Ren et al., 2003; Khan et al., 2008; Petäjä et al., 2009; Stone et al., 2012). For an OH concentration of 1×10^5 molecule cm⁻³ (0.004 ppt), with the average O₃ concentration of 15 ppb at 7 am, the reaction rate of monoterpene + OH was about 0.25 times as high as that of monoterpene + O₃. If the OH concentration was up to 1×10^6 molecule cm⁻³ (0.04 ppt) at 7 am, the reaction rate of monoterpene with OH radical was 2.5 times higher than that of monoterpene with O₃ according to the calculations. In other words, both oxidants are likely to be of importance at this time. For the evening peak of the less oxidized monoterpene oxidation products at 8 pm, the relative importance of O₃ and OH radical in monoterpene chemistry changed due to the lower OH concentration. With the average O₃ concentration of ~20 ppb and OH concentration of 0.012 ppt at 8 pm, ~~the reaction rates of monoterpenes with O₃ and OH radical were at the similar level. a similar analysis as above resulted in O₃ reactions being 5-50 times more important than OH radical reactions with monoterpenes, indicating that the evening peaks are mainly from ozonolysis.~~ Compared to other compounds, the evening peak of C₉H₁₄O, C₁₀H₁₆O, C₁₀H₁₈O, and C₁₀H₁₈O₂ extended over midnight. C₉H₁₄O has been found to be one of the main products formed in the ozonolysis reactions of monoterpenes (Atkinson and Arey, 2003). O₃-initiated oxidation with extremely high monoterpene levels might be responsible for the high concentration of C₉H₁₄O at night. Camphor (C₁₀H₁₆O), linalool (C₁₀H₁₈O), and linalool oxide (C₁₀H₁₈O₂) can be emitted by leaves and flowers (Corchnoy et al., 1992; Lavy et al., 2002). Therefore, direct emissions from vegetation in the Landes forest may contribute to the high mixing ratios of these compounds during night. With strong photochemical oxidations during the day, the diurnal cycles of the more oxidized compounds were characterized with a broad daytime distribution peaking between 2:00 pm and 4:00 pm UTC.

409 To date the oxidation processes of sesquiterpenes have been rarely investigated despite its potential significance in
410 new particle formation and SOA formation (Bonn and Moortgat, 2003; Winterhalter et al., 2009). In this study, various
411 sesquiterpene oxidation products were observed, mainly including $C_{14}H_{22}O_n$, $C_{15}H_{22}O_n$, and $C_{15}H_{24}O_n$ ($n=1\sim6$), providing the
412 possibility to explore the oxidations of sesquiterpenes in the atmosphere. As shown in Fig. 9 and Fig. S134-142, with the
413 increase of oxygen numbers, sesquiterpene oxidation products displayed similar variations in their diurnal profiles with
414 monoterpene oxidation products. The less oxidized products with 1 to 3 oxygen peaked both in the morning and in the evening,
415 and the more oxidized compounds had a broad presence throughout the day. These results indicate the similar oxidation
416 processes of sesquiterpenes with monoterpenes in the Landes forest.

417 3.4.3 Terpene-derived organic nitrates

418 Organic nitrates have been shown to represent a large fraction of submicron aerosol nitrate at both urban and rural sites in
419 Europe (Kiendler-Scharr et al., 2016). During daytime, the reaction of peroxy radicals with NO can lead to the formation of
420 organic nitrates. At night, NO_3 radicals from the oxidation of NO_2 by O_3 , can also react with unsaturated compounds mostly
421 coming from BVOCs to generate organic nitrates (Ayres et al., 2015). In this study, the less oxidized organic nitrates from
422 monoterpene oxidations presented a distinct morning peak at 7 am (Fig. 11; Fig. S175-186), which can come from O_3 - and
423 OH-initiated monoterpene oxidations in the presence of NO_x . In addition, both isoprene- and monoterpene-derived organic
424 nitrates showed evening peaks at around 8 pm (Fig. 10, Fig. S153-164). Using monoterpenes as an example, the relative roles
425 of O_3 , OH radical, and NO_3 radical in the nighttime formation of monoterpene-derived organic nitrates were evaluated by
426 calculating the corresponding reaction rate (R):

$$427 R_{MT+O_3} = k_{MT+O_3}[MT][O_3] \quad (3)$$

$$428 R_{MT+OH} = k_{MT+OH}[MT][OH] \quad (4)$$

$$429 R_{MT+NO_3} = k_{MT+NO_3}[MT][NO_3] \quad (5)$$

430 where k is the reaction rate coefficient of monoterpenes with O_3 , OH radical or NO_3 radical, and [MT], $[O_3]$, [OH] or $[NO_3]$ is
431 the concentration of monoterpenes, O_3 , OH radical or NO_3 radical.

432 Taking the peak concentration of monoterpene-derived organic nitrates at 8 pm as an example, the concentration of NO_3 radical
433 was calculated by assuming a steady state between its production from O_3 and NO_2 and its removal by oxidation reactions and
434 losses. The details have been described by Allan et al. (2000) and Peräkylä et al. (2014). With the high O_3 scavenging by
435 monoterpenes in the evening, the estimated concentration of NO_3 radical was 0.017 ppt. Using $k_{MT+O_3} = 6.9 \times 10^{-17} \text{ cm}^3$
436 $\text{molecule}^{-1} \text{ s}^{-1}$ and $k_{MT+NO_3} = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ taken from Peräkylä et al. (2014), the reaction rate of monoterpenes
437 with O_3 was ~10 times higher than that of monoterpenes with NO_3 radicals. However, while ozonolysis was likely to dominate
438 the overall oxidation of monoterpenes, the organic nitrate formation from O_3 -initiated oxidation may still be much lower than
439 those from NO_3 -initiated oxidations, depending on what fraction of RO_2 radicals were reacting with NO_x . The relative
440 importance of O_3 and OH radical in monoterpene chemistry at this time was the same as discussed in Sect. 3.4.2.

441 4. Conclusions

442 This work presented the deployment of the new state-of-the-art Vocus PTR-TOF in the French Landes forest during the
443 CERVOLAND campaign. The Vocus PTR-TOF capabilities are evaluated for the first time in the actual ambient environment
444 by the identification of the observed gas-phase molecules. With the improved detection efficiency and measurement precision
445 compared to the conventional PTR instruments, multiple hydrocarbons with carbon numbers varying from 3 to 20 were
446 observed as well as various VOCs oxidation products. Hydrocarbon signals were dominated by monoterpenes and their major
447 fragment ions (e.g., $C_6H_8H^+$) within the instrument, consistent with high monoterpene emissions in the Landes forest. In general,

448 most hydrocarbon molecules and the less oxidized compounds were characterized with high signals at night, whereas the more
449 oxidized compounds exhibited elevated intensity during the day.

450 To demonstrate the importance of Vocus PTR-TOF application in atmospheric science study, the characteristics of
451 terpenes and their oxidation products were investigated. In addition to the observation of isoprene, monoterpenes, and
452 sesquiterpenes, this study presented the ambient characteristics of the rarely recorded diterpenes, which are traditionally
453 considered as non-volatile species in the atmosphere. On average, the concentration of diterpenes was 1.7 ppt in the Landes
454 forest, which was hundred to thousand times lower than that of monoterpenes (6.0 ppb) and sesquiterpenes (64.5 ppt). However,
455 considering their low vapor pressure and high reactivity, diterpenes may potentially play an important part in atmospheric
456 chemistry. The diurnal variations of diterpenes showed the maximum peak at night and low levels during the day, similar to
457 those of monoterpenes and sesquiterpenes.

458 With strong photochemical oxidations of terpenes during the day, the more oxidized terpene reaction products were
459 observed with a broad daytime peak, whereas the less oxidized terpene reaction products showed peak concentrations in the
460 early morning or/and in the evening. By calculating the reaction rates of terpenes with the main oxidants, OH radical, O₃, and
461 NO₃ radical, the contributions of different formation pathways to terpene oxidations were evaluated. The morning and evening
462 peaks of non-nitrate terpene reaction products were contributed by both O₃- and OH-induced terpene oxidations. ~~For the~~
463 ~~evening peaks of non-nitrate terpene oxidation products, terpene ozonolysis played an increasing role due to the lower OH~~
464 ~~concentration at night.~~ For the formation of terpene-derived organic nitrates, the relative importance of O₃-, OH-, and NO₃-
465 driven oxidation pathways were more difficult to evaluate. Overall, we have shown that the Vocus PTR-TOF is able to detect
466 a very broad coverage of compounds, from VOCs precursors to various oxidation products. Therefore, the application of the
467 Vocus PTR-TOF in atmospheric sciences will be fundamental in understanding the chemical evolution of VOCs in the
468 atmosphere and their roles in air quality and climate issues.

469 **Author contributions**

470 ME and MR conceived the study. MR, LH, PF, EV, and EP conducted the field measurements. HL carried out the data analysis.
471 MR, PR, KD, JK, DW, MK, ME, and FB participated the data analysis. HL wrote the paper with inputs from all coauthors.

472 **Competing interests**

473 The authors declare that they have no conflict of interest.

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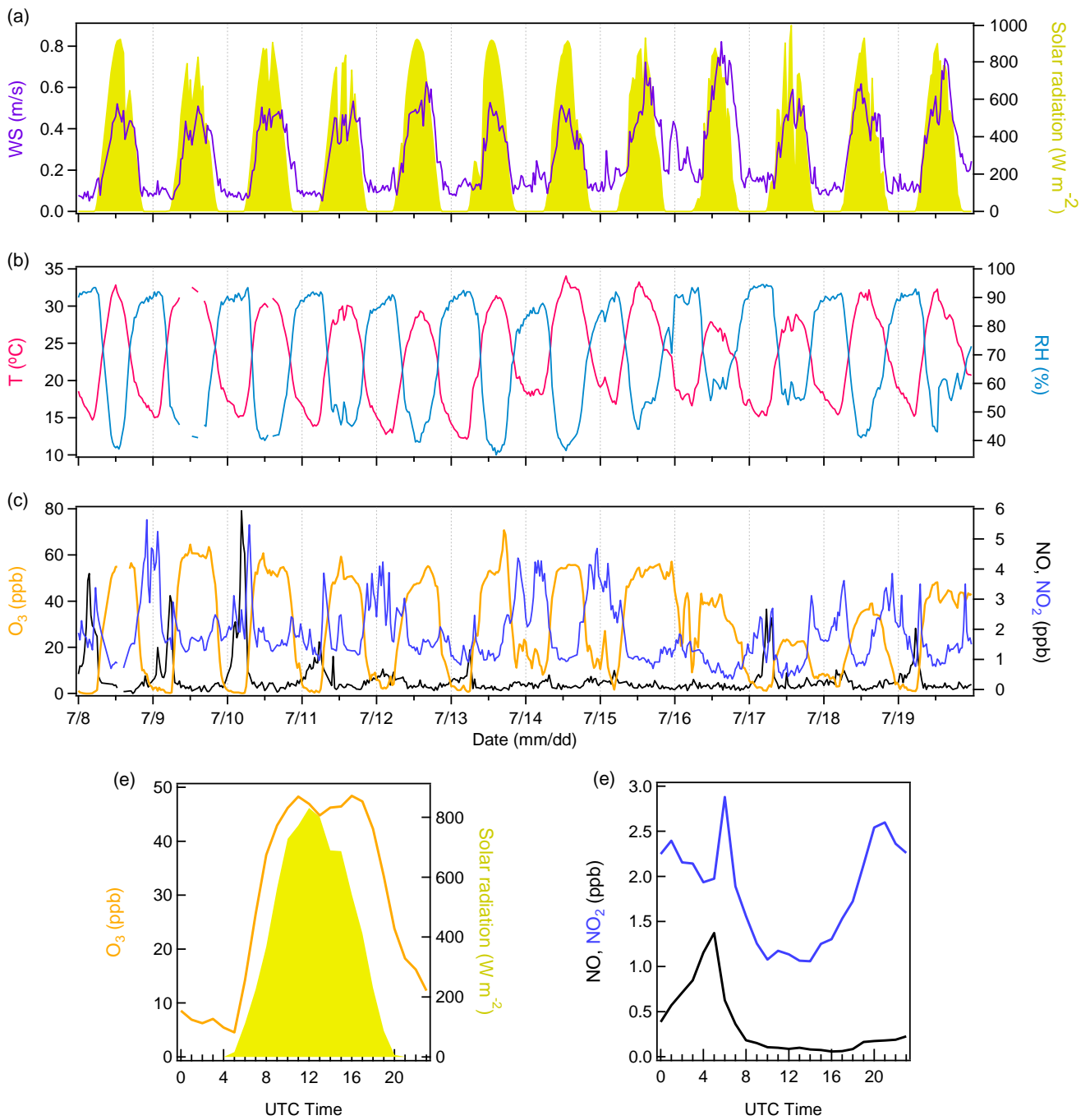
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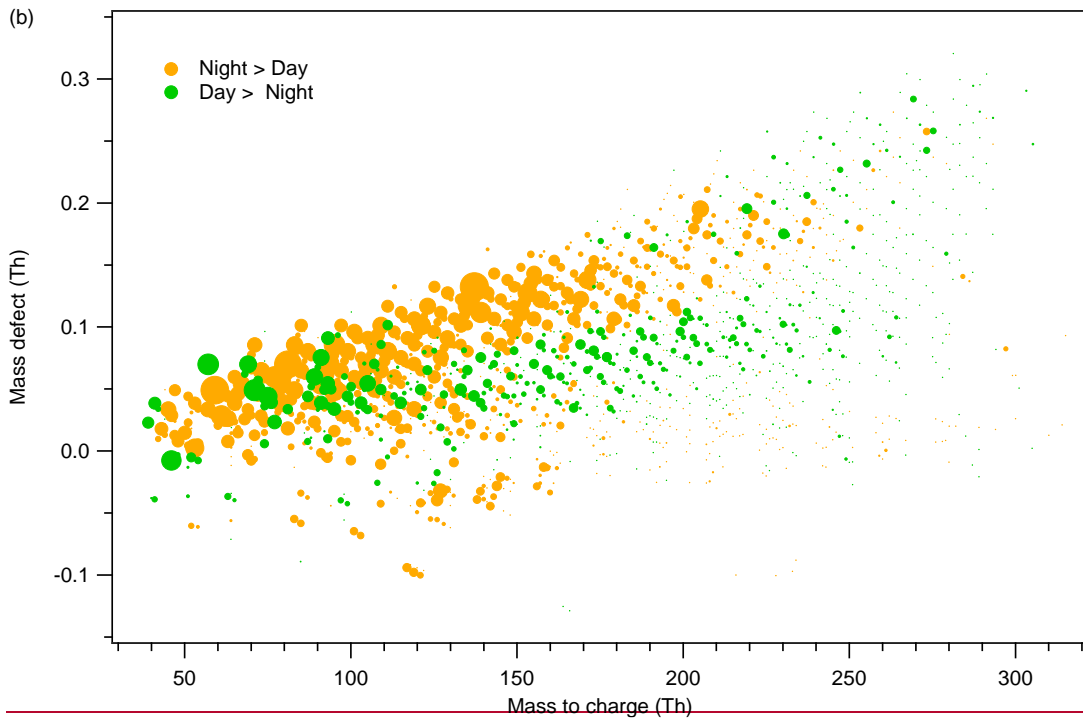
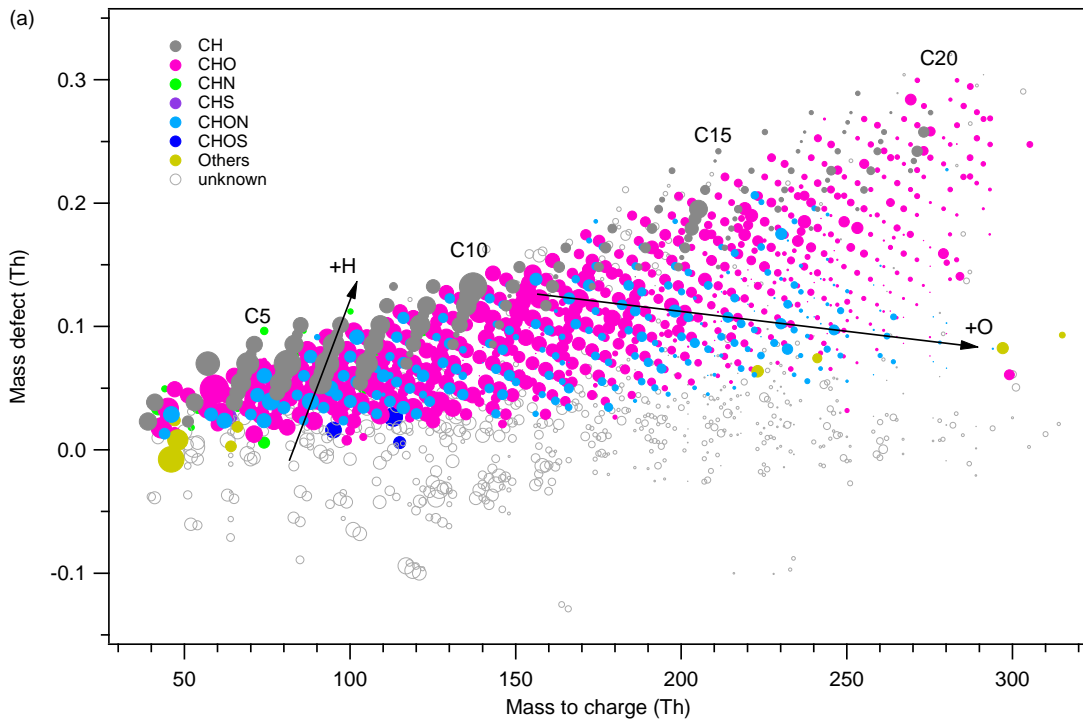
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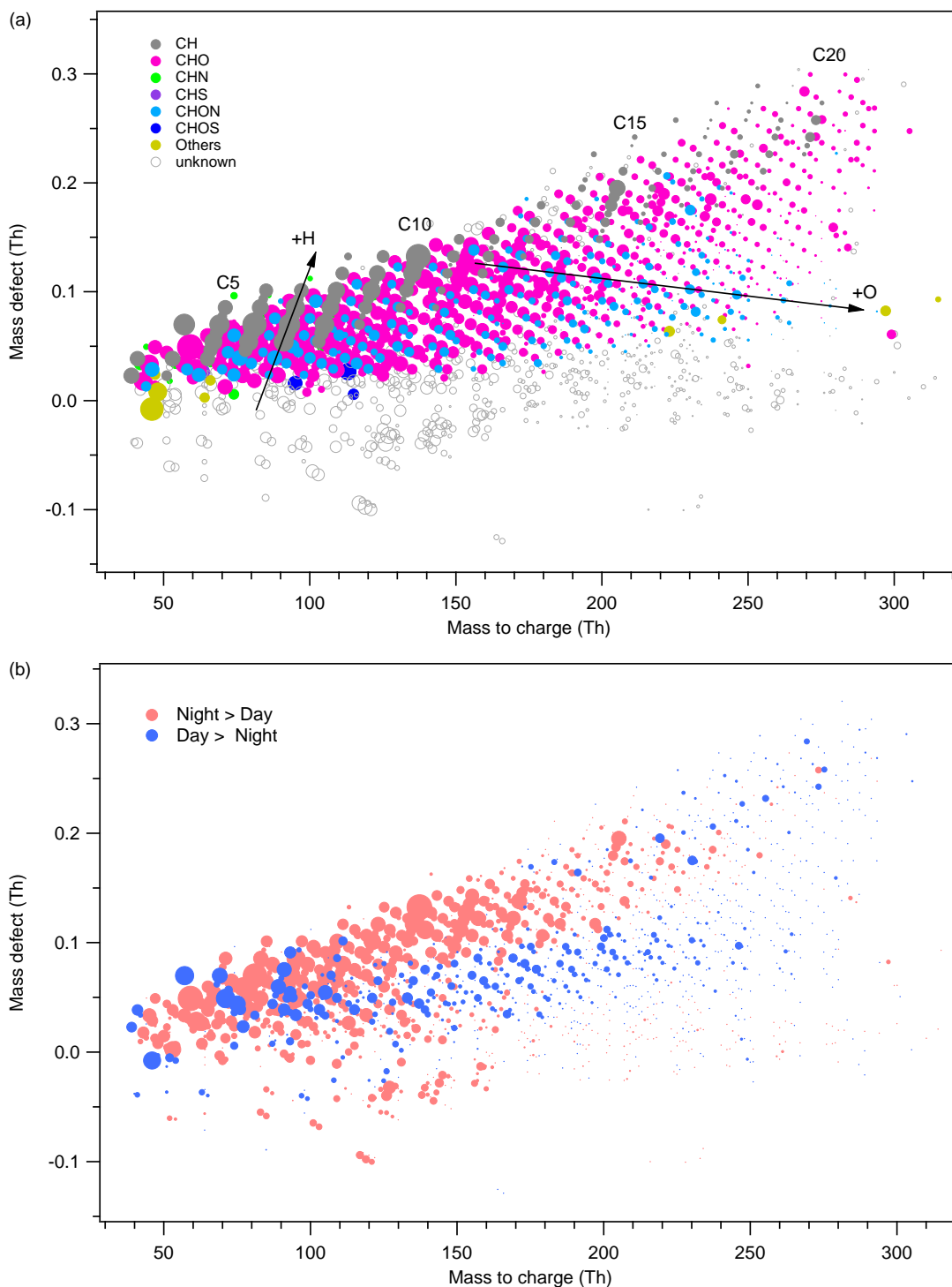
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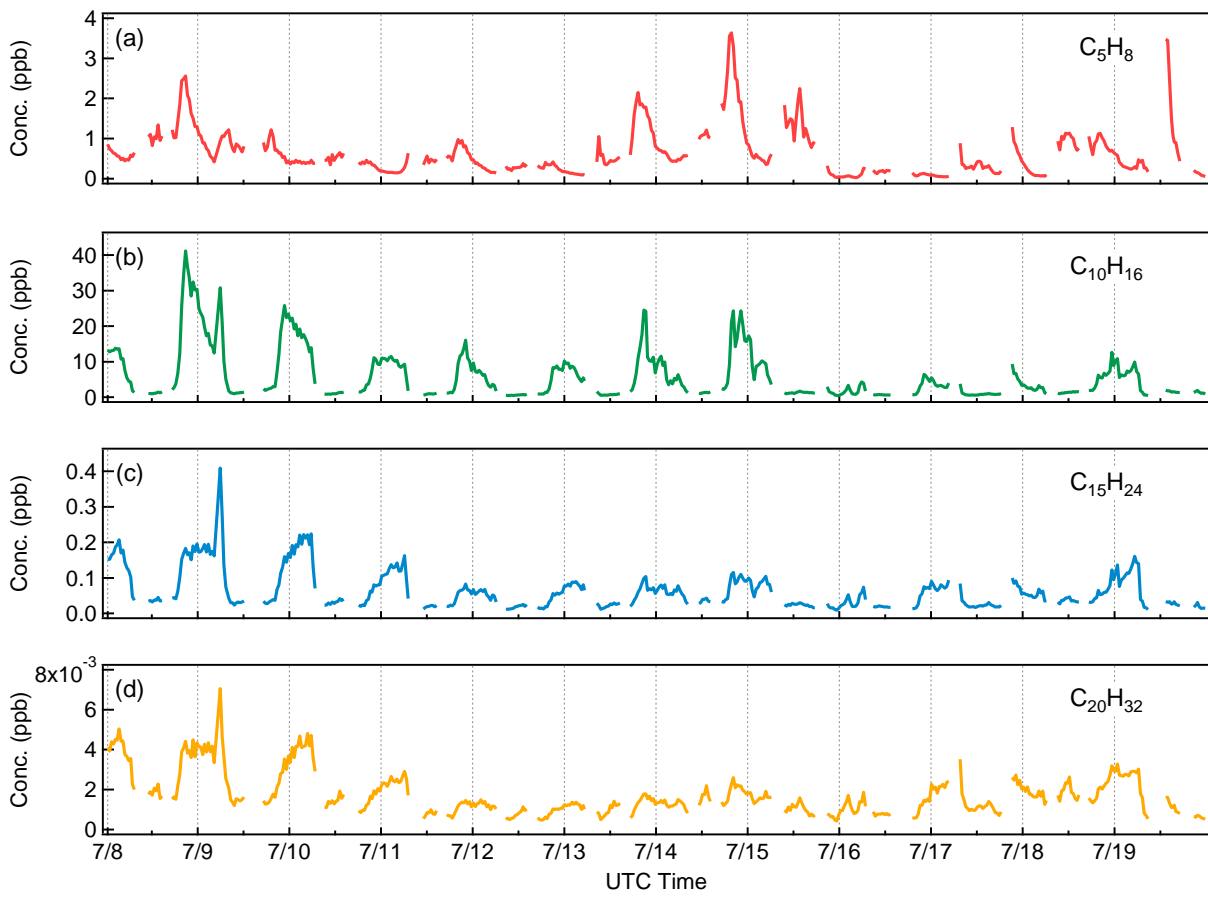
843 **Figure 1. Variations of meteorological conditions and trace gases. (a) Time series of wind speed and solar radiation. (b)**
 844 **Time series of temperature and relative humidity. (c) Time series of O_3 , NO, and NO_2 . (d) Diurnal cycles of O_3 and**
 845 **solar radiation. (e) Diurnal cycles of NO and NO_2 .**





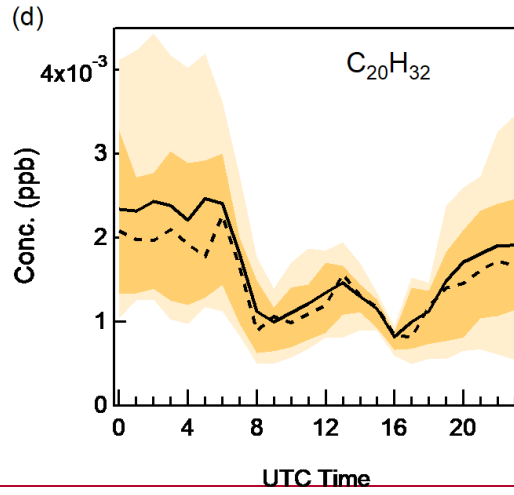
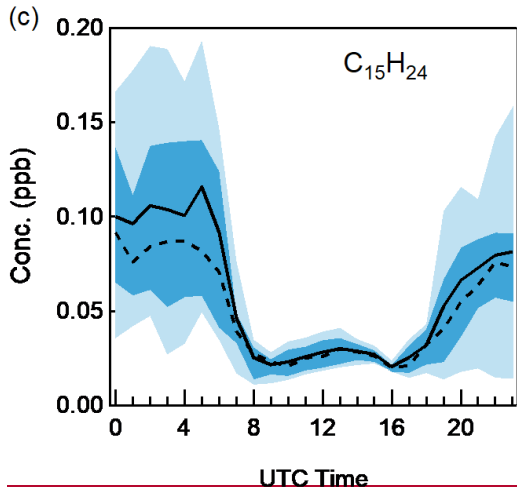
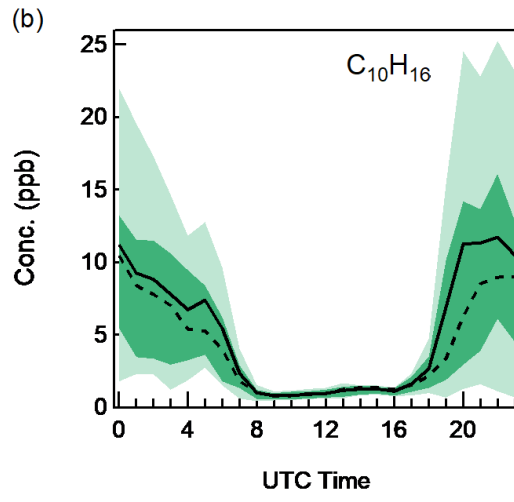
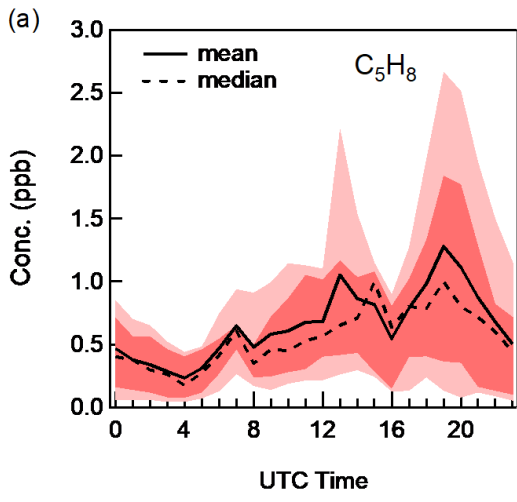
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848 **Figure 2. Mass defect plot of the ions identified by high-resolution analysis of Vocus PTR-TOF data set. The x-axis**
 849 **shows the mass to charge ratio and the y-axis shows the mass defect, which is the deviation of the exact mass**
 850 **from the nominal mass. Data points in (a) are color-coded by ion family (CH, CHO, CHN, CHS, CHON, CHOS) and**
 851 **sized by the logarithm of peak area. Data points in (b) are shown in pink when signals are higher during**
 852 **nighttime and in blue when daytime signal is higher. The size corresponds to the difference of daytime and**
 853 **nighttime signal for the molecule. It should be noted that ions < 35 Th are detected at a much-reduced efficiency due**
 854 **to a high-pass band filter in the BSQ.**

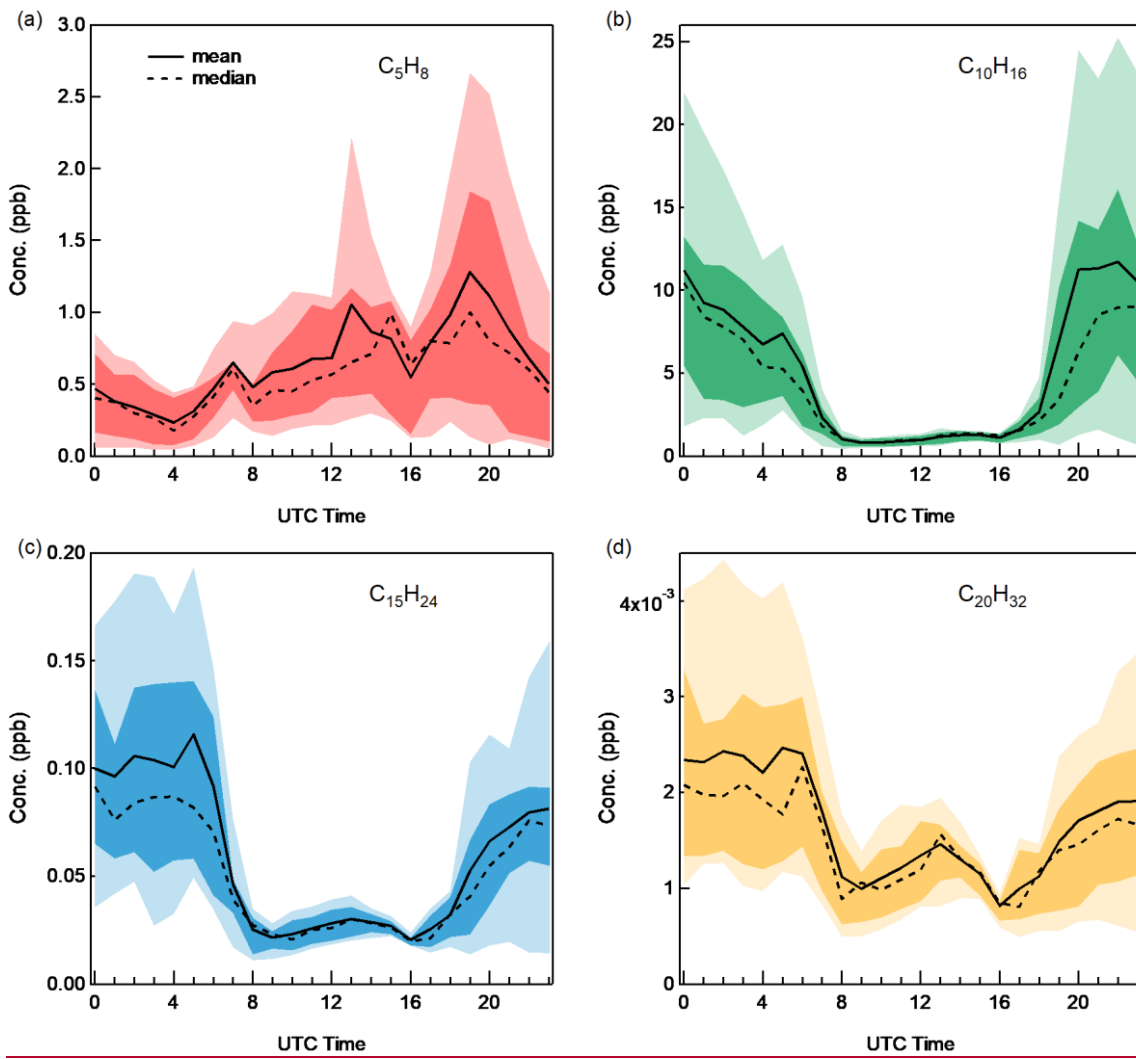


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856 **Figure 3. Time series of (a) C_5H_8 , (b) $C_{10}H_{16}$, (c) $C_{15}H_{24}$, and (d) $C_{20}H_{32}$.**



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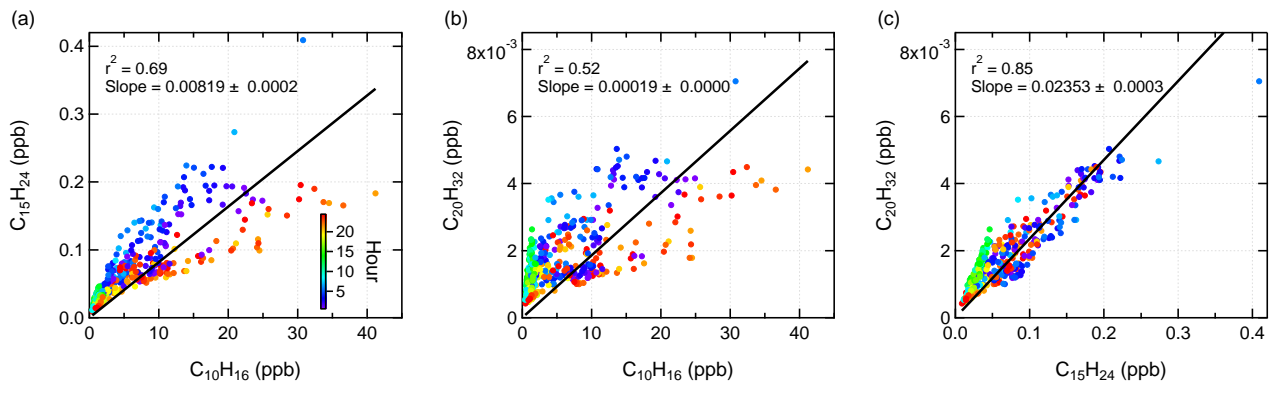


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Figure 4. Diurnal cycles of (a) C_5H_8 , (b) $C_{10}H_{16}$, (c) $C_{15}H_{24}$, and (d) $C_{20}H_{32}$, with the 10th, 25th, 75th, and 90th percentiles shown in the shaded area.

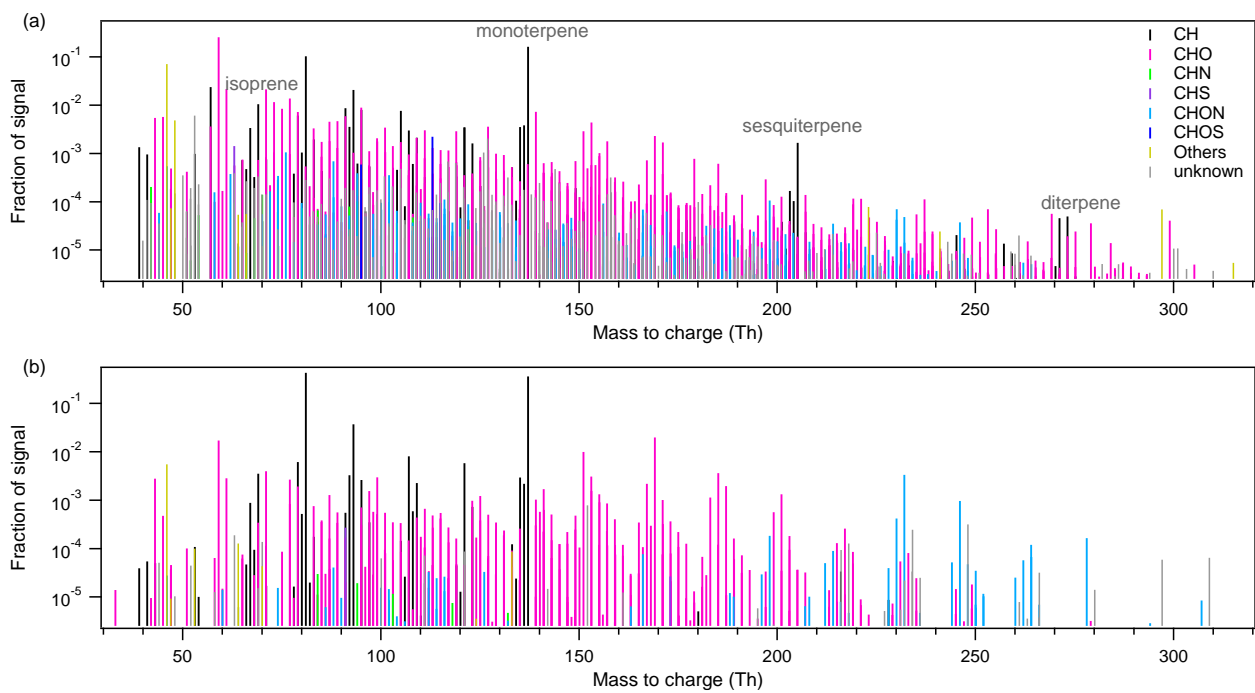


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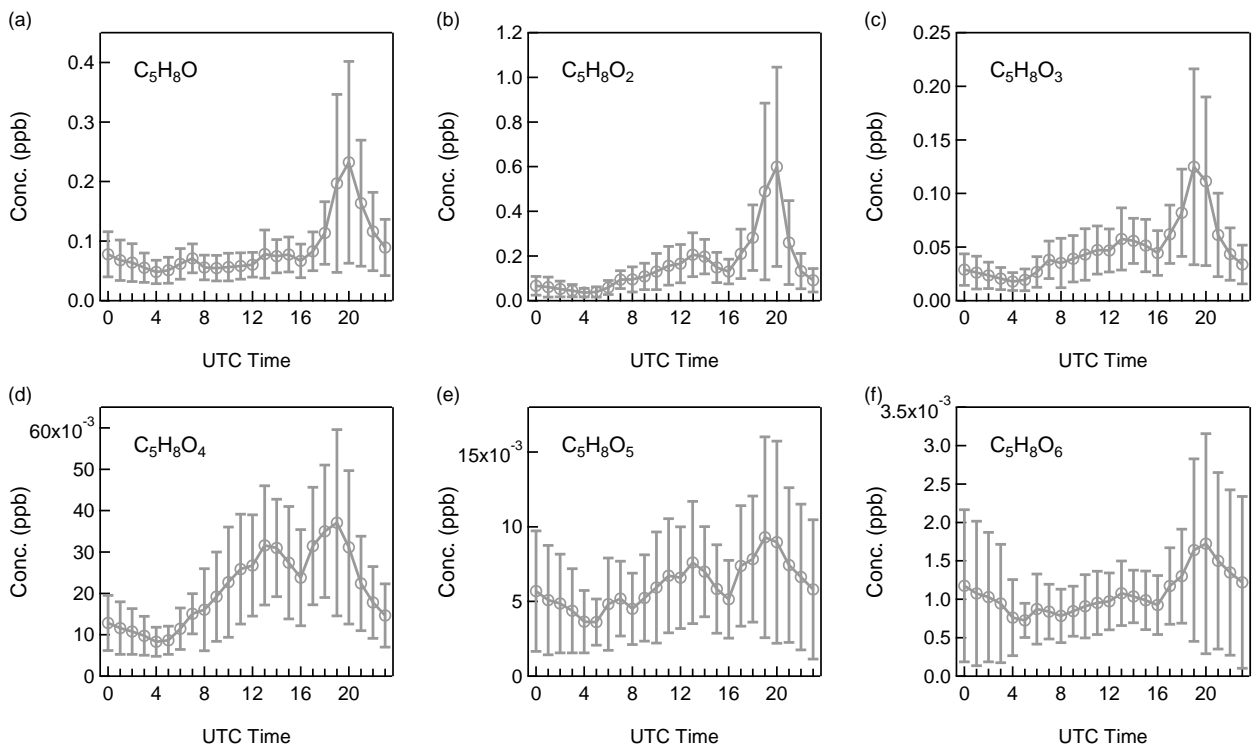
Figure 5. Scatter plots of (a) $C_{15}H_{24}$ vs. $C_{10}H_{16}$, (b) $C_{20}H_{32}$ vs. $C_{10}H_{16}$, and (c) $C_{20}H_{32}$ vs. $C_{15}H_{24}$, colored by time of the day.



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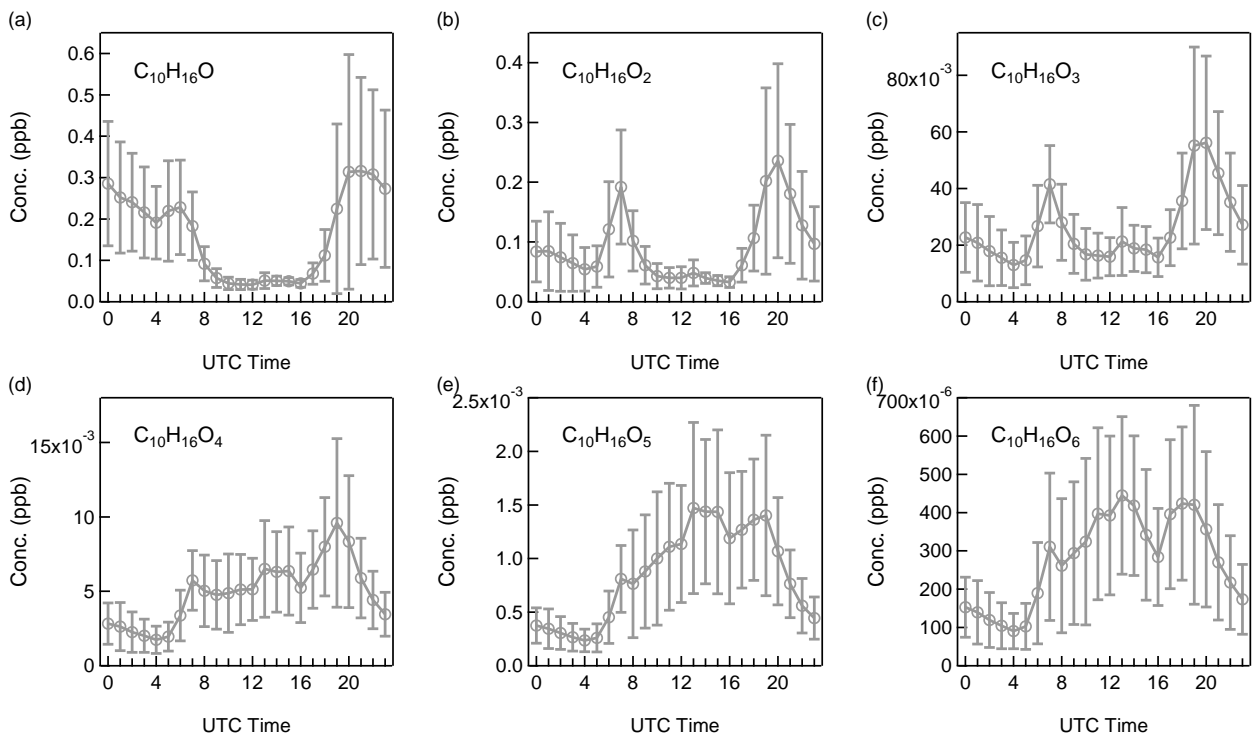
865 **Figure 6. Comparison of ambient average high-resolution mass spectra with those from α -pinene oxidation experiments**

866 **in the COALA chamber. (a) ambient observations in the Landes Forest; (b) α -pinene ozonolysis with NO_x .**



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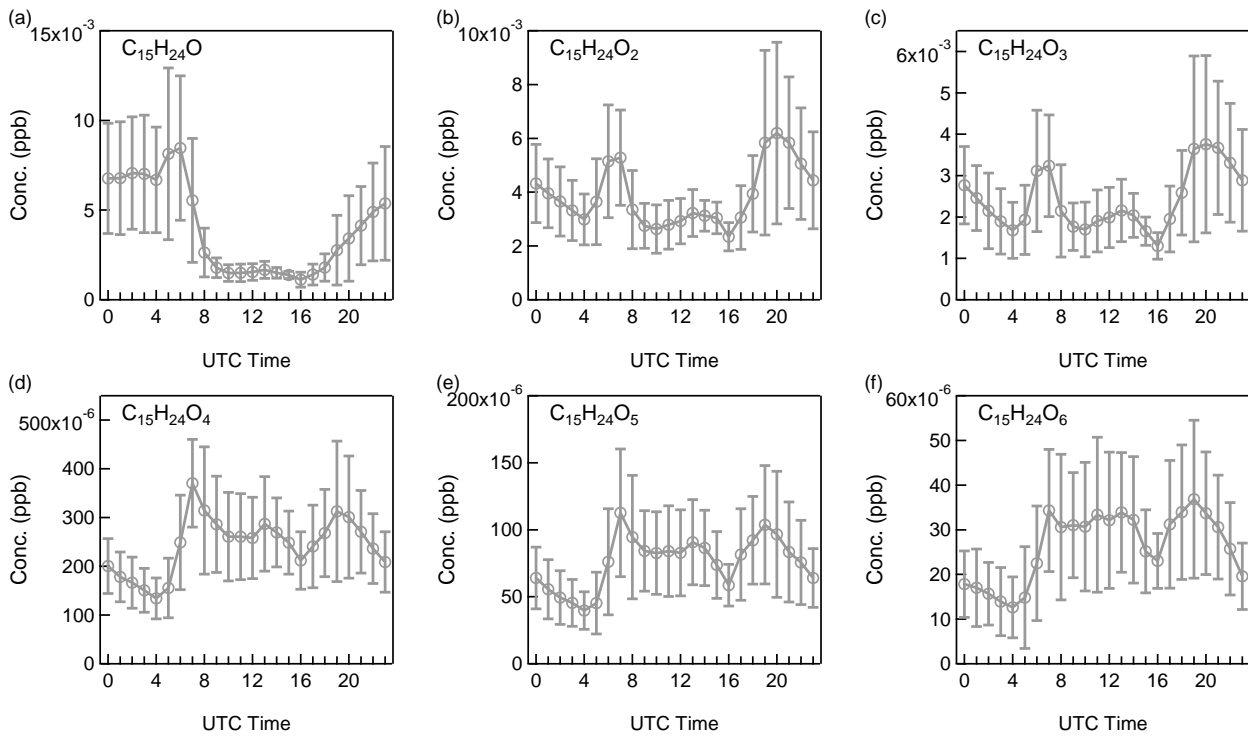
868 **Figure 7. Diurnal patterns of non-nitrate isoprene oxidation products: (a) C_5H_8O , (b) $C_5H_8O_2$, (c) $C_5H_8O_3$, (d) $C_5H_8O_4$,**
 869 **(e) $C_5H_8O_5$, and (f) $C_5H_8O_6$.**



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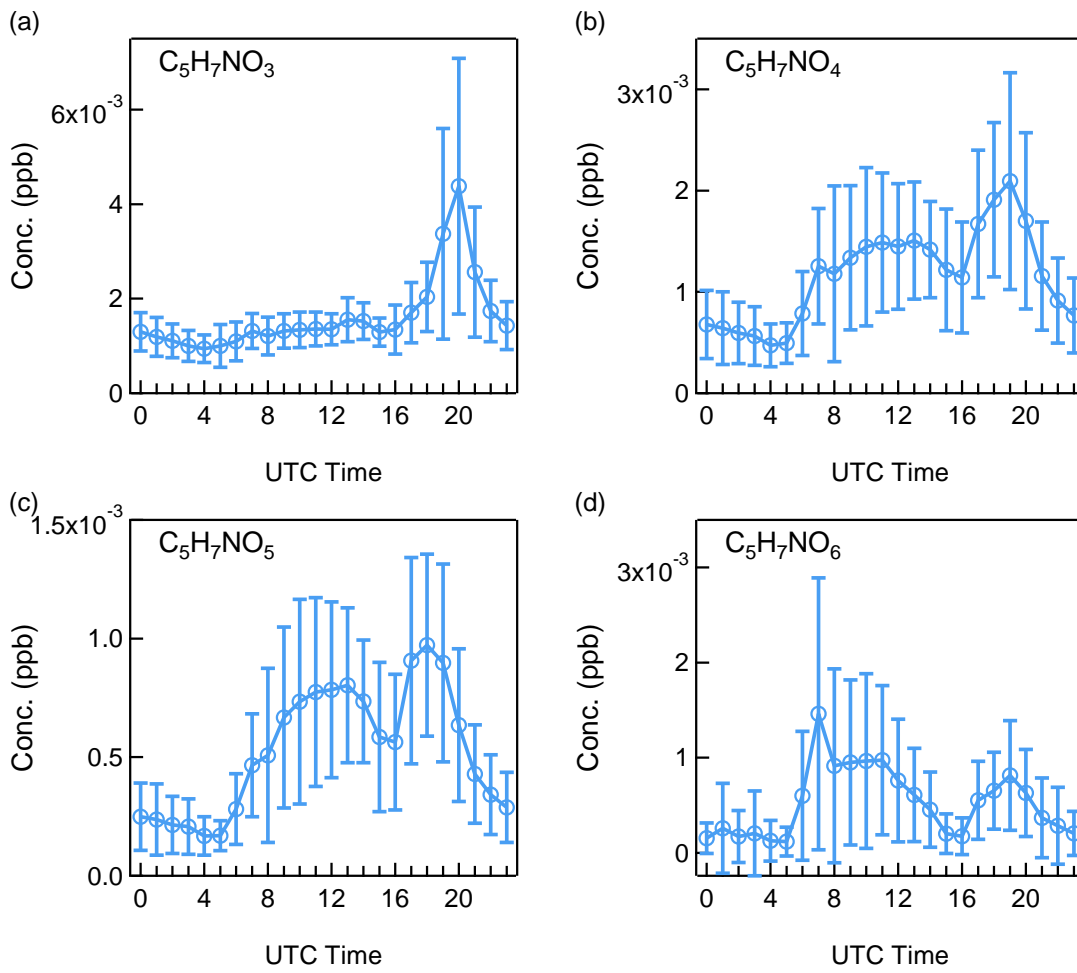
871 **Figure 8. Diurnal patterns of non-nitrate monoterpene oxidation products: (a) $C_{10}H_{16}O$, (b) $C_{10}H_{16}O_2$, (c) $C_{10}H_{16}O_3$, (d)**

872 **$C_{10}H_{16}O_4$, (e) $C_{10}H_{16}O_5$, and (f) $C_{10}H_{16}O_6$.**



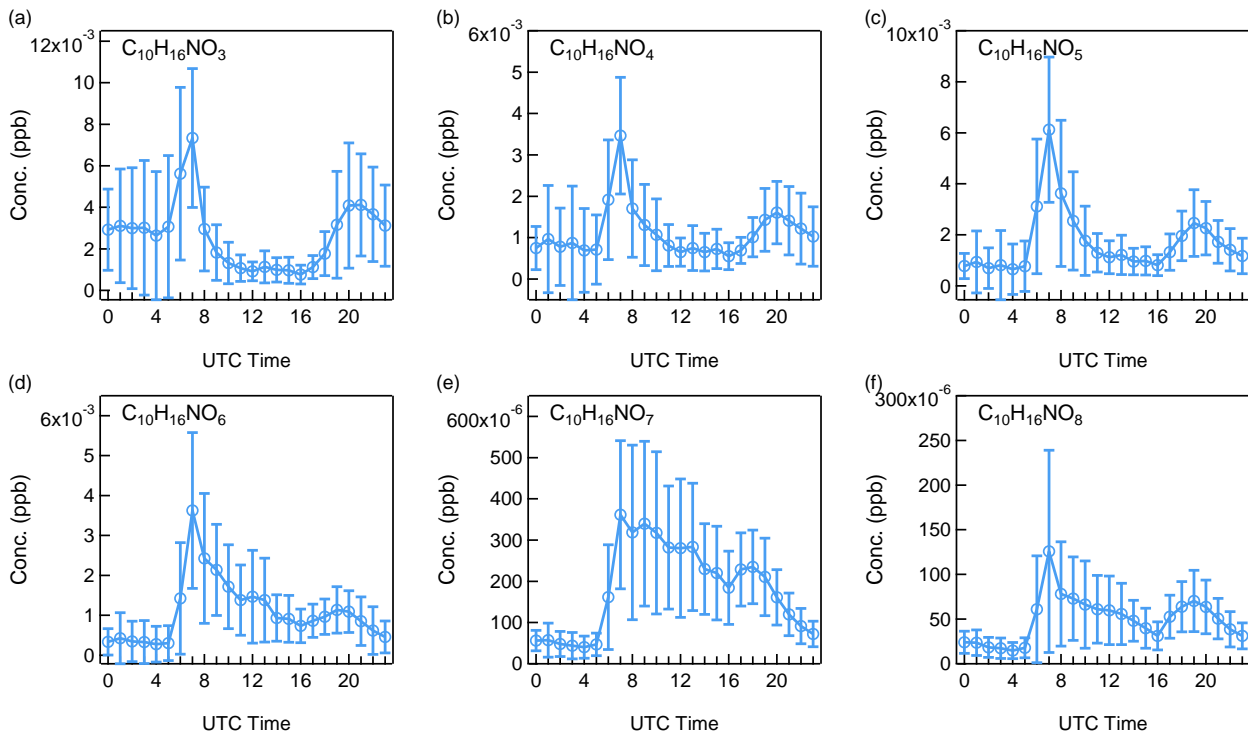
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874 **Figure 9. Diurnal patterns of non-nitrate sesquiterpene oxidation products: (a) $C_{15}H_{24}O$, (b) $C_{15}H_{24}O_2$, (c) $C_{15}H_{24}O_3$, (d)**
 875 **$C_{15}H_{24}O_4$, (e) $C_{15}H_{24}O_5$, and (f) $C_{15}H_{24}O_6$.**



876

877 **Figure 10. Diurnal patterns of isoprene-derived organic nitrates: (a) $C_5H_7NO_3$, (b) $C_5H_7NO_4$, (c) $C_5H_7NO_5$, and (d)**
 878 **$C_5H_7NO_6$.**



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880 **Figure 11. Diurnal patterns of monoterpene-derived organic nitrates: (a) $C_{10}H_{15}NO_3$, (b) $C_{10}H_{15}NO_4$, (c) $C_{10}H_{15}NO_5$, (d)**
 881 **$C_{10}H_{15}NO_6$, (e) $C_{10}H_{15}NO_7$, and (f) $C_{10}H_{15}NO_8$.**

Terpenes and their oxidation products in the French Landes forest: insight from Vocus PTR-TOF measurements

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Detection of the high C₄H₉⁺ signals

One possible contribution to the detected C₄H₉⁺ could be the protonated butene, which is emitted by biogenic or anthropogenic sources (Goldstein et al., 1996; Hellén et al., 2006; Zhu et al., 2017). In addition, C₄H₉⁺ ions are very common fragments of many VOCs in PTR instruments and the peaks are prominent in the mass spectra (Pagonis et al., 2019). The fragmentation of butanol also produces significant C₄H₉⁺ signals. Like many other alcohols, butanol can easily lose an OH during ionization in PTR sources (Spanel and Smith, 1997). During the measurements at the Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II) site in Hyytiälä Finland, Schallhart et al. (2018) concluded that C₄H₉⁺ signal detected by PTR-TOF mainly came from butanol used by aerosol instruments, i.e., condensation particle counters (CPCs). In this study, CPCs using butanol to measure the particle concentration were also deployed at the site. While the exhaust air emitted from these collocated instruments was filtered using charcoal denuder, we cannot exclude the contribution of butanol to the identified C₄H₉⁺ signal. The spiky peaks in the time series of C₄H₉⁺ compound also indicated the influence of butanol (Fig. S19). Finally, the green leaf volatiles (GLV), a group of six-carbon aldehyde, alcohols and their esters which can be directly released by the plants, have been found to fragment at *m/z* 57 inside the PTR instruments (Rinne et al., 2005; Pang, 2015) and may also contribute to the observed C₄H₉⁺ signal.

Calculation of the steady-state OH concentration from alkene ozonolysis

If the competition between OH production and removal processes leads to a steady station of OH formation, the OH concentration can be calculated using the following equation (Dusanter et al., 2008):

$$[OH]_{ss} = \frac{k_{O_3+VOC}\alpha[O_3][alkene]}{k_{OH+VOC}[alkene] + k_{OH+O_3}[O_3]}$$

where k_{O_3+VOC} is the rate constant for O₃+alkene reaction with an OH yield of α , k_{OH+VOC} is the rate constant for OH+alkene reaction, k_{OH+O_3} is the rate constant for OH+ O₃ reaction. The rate constant of OH and O₃ reactions was obtained from Atkinson et al. (1992). At night, alkene concentrations in the Landes forest were dominated by monoterpenes, mainly α - and β -pinene (Riba et al., 1987; Simon et al., 1994). For the calculation of OH concentration, the loss of OH from reaction with O₃ was neglected, as it was much smaller than the loss of OH due to its reaction with monoterpenes (Gill and Hites, 2002). The rate constant of O₃ and monoterpene reactions was taken from Hakola et al. (2012), and the OH formation yield from O₃ and monoterpene reactions was obtained from Alicke et al. (2003). Finally, we assumed the equal contribution of α - and β -pinene to OH formation through alkene ozonolysis in this study. Hence, using an O₃ concentration of ~20 ppb at 8 pm, the OH concentration is estimated to be 0.012 ppt.

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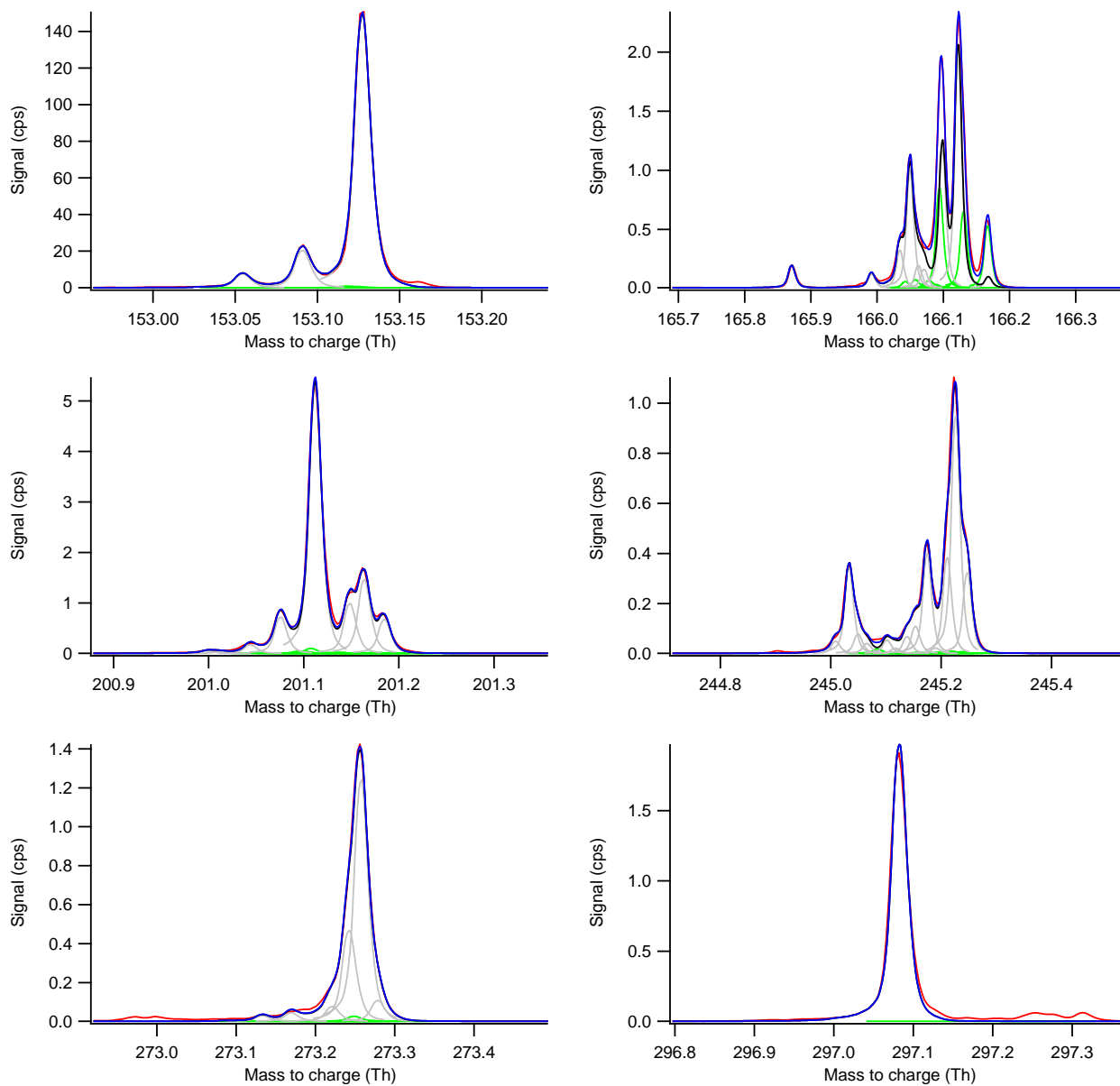


Figure S1. Examples of peak identification with the LTOF mass analyzer.

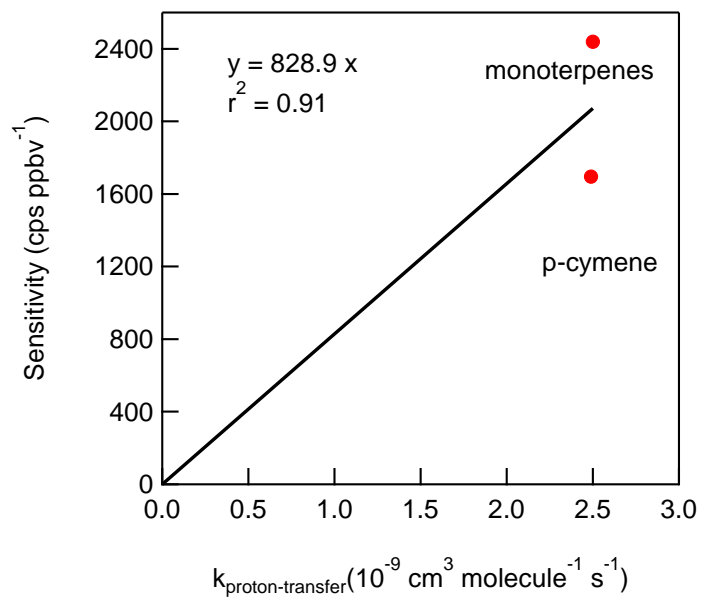


Figure S2. The built empirical relationship between the sensitivities and the proton-transfer reaction rate coefficients (k) using the calibrated data of monoterpenes and *p*-cymene: Sensitivity (cps ppbv⁻¹) = 828.9 \times k .

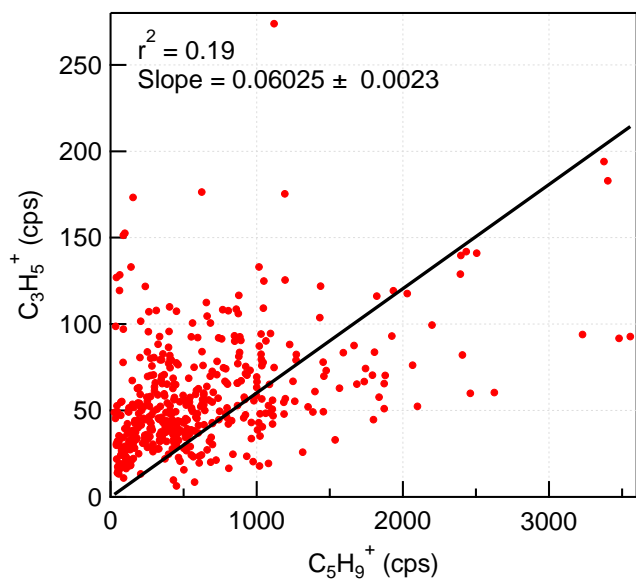


Figure S3. Correlation of the time variations between $C_3H_5O^+$ and $C_5H_9^+$ signals.

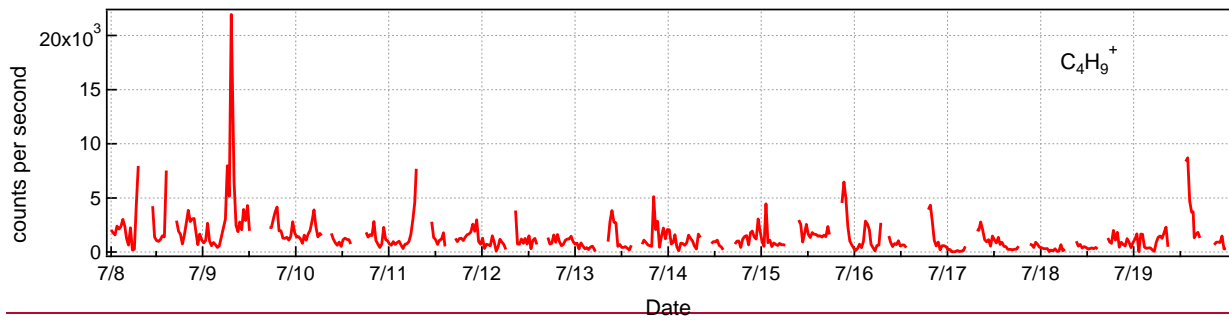


Fig. S2. Time series of the identified $C_4H_9^+$.

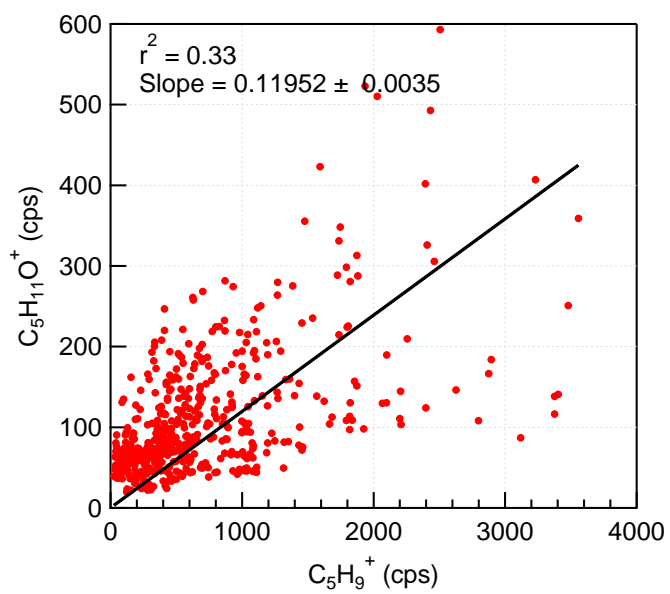


Figure S4. Correlation of the time variations between $C_5H_{11}O^+$ and $C_5H_9^+$ signals.

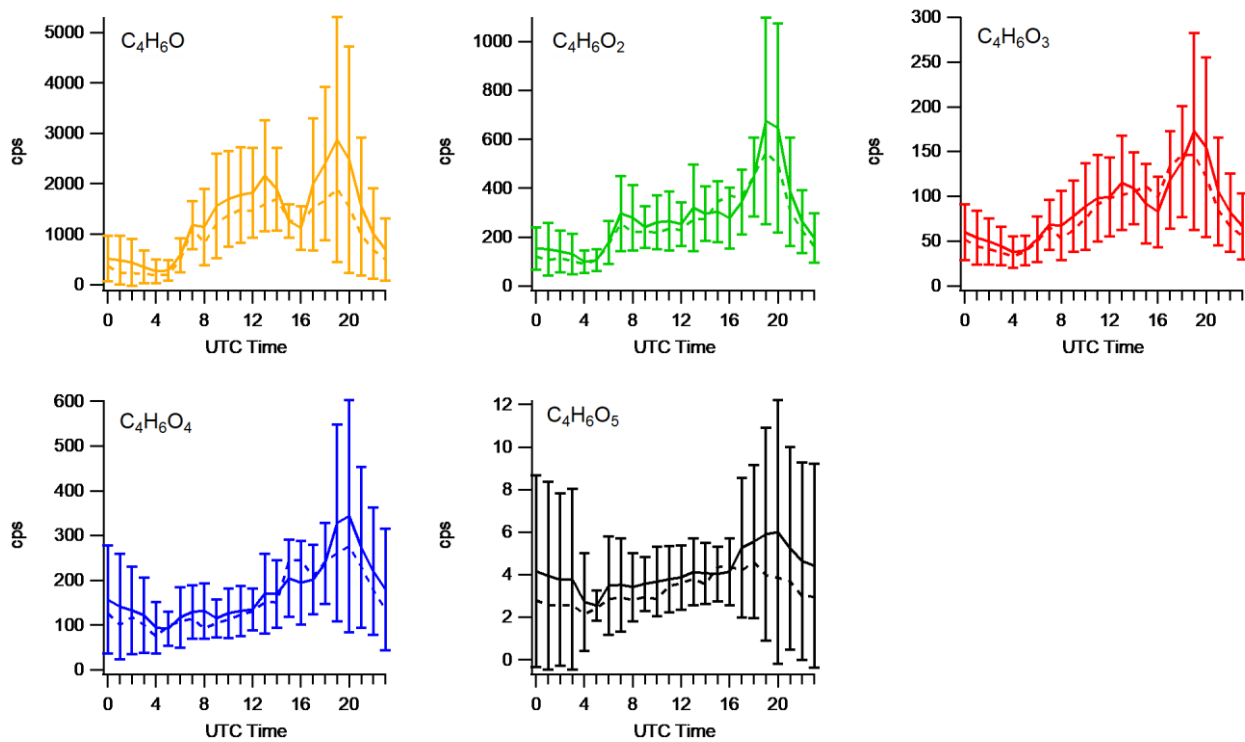


Figure S53. Diurnal patterns of non-nitrate isoprene oxidation products: (a) C_4H_6O , (b) $C_4H_6O_2$, (c) $C_4H_6O_3$, (d) $C_4H_6O_4$, and (e) $C_4H_6O_5$.

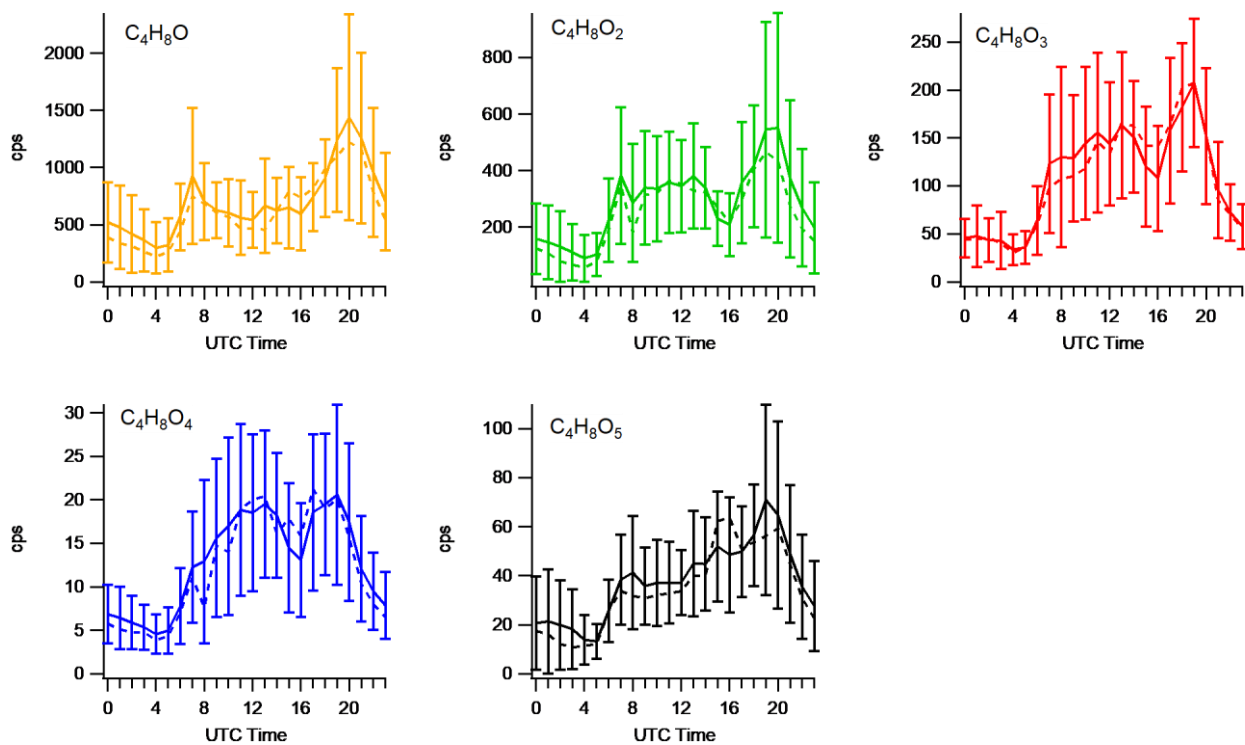


Figure S64. Diurnal patterns of non-nitrate isoprene oxidation products: (a) C_4H_8O , (b) $C_4H_8O_2$, (c) $C_4H_8O_3$, (d) $C_4H_8O_4$, and (e) $C_4H_8O_5$.

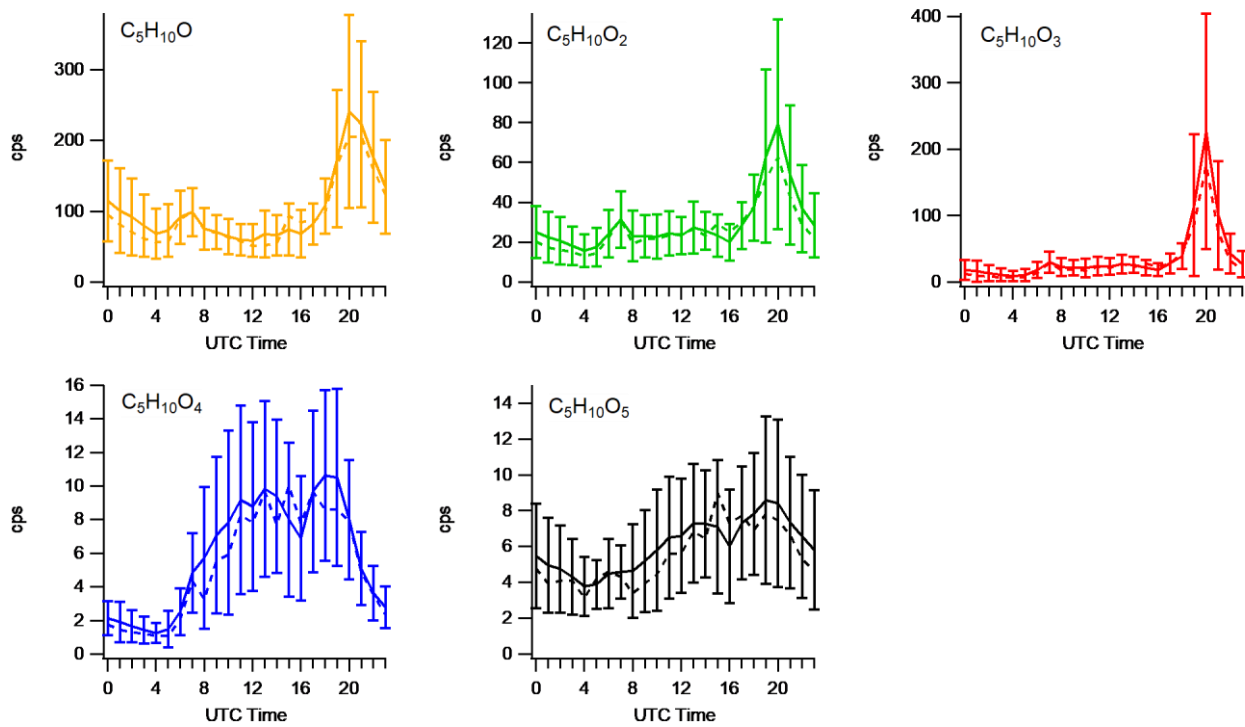


Figure S75. Diurnal patterns of non-nitrate isoprene oxidation products: (a) $C_5H_{10}O$, (b) $C_5H_{10}O_2$, (c) $C_5H_{10}O_3$, (d) $C_5H_{10}O_4$, and (e) $C_5H_{10}O_5$.

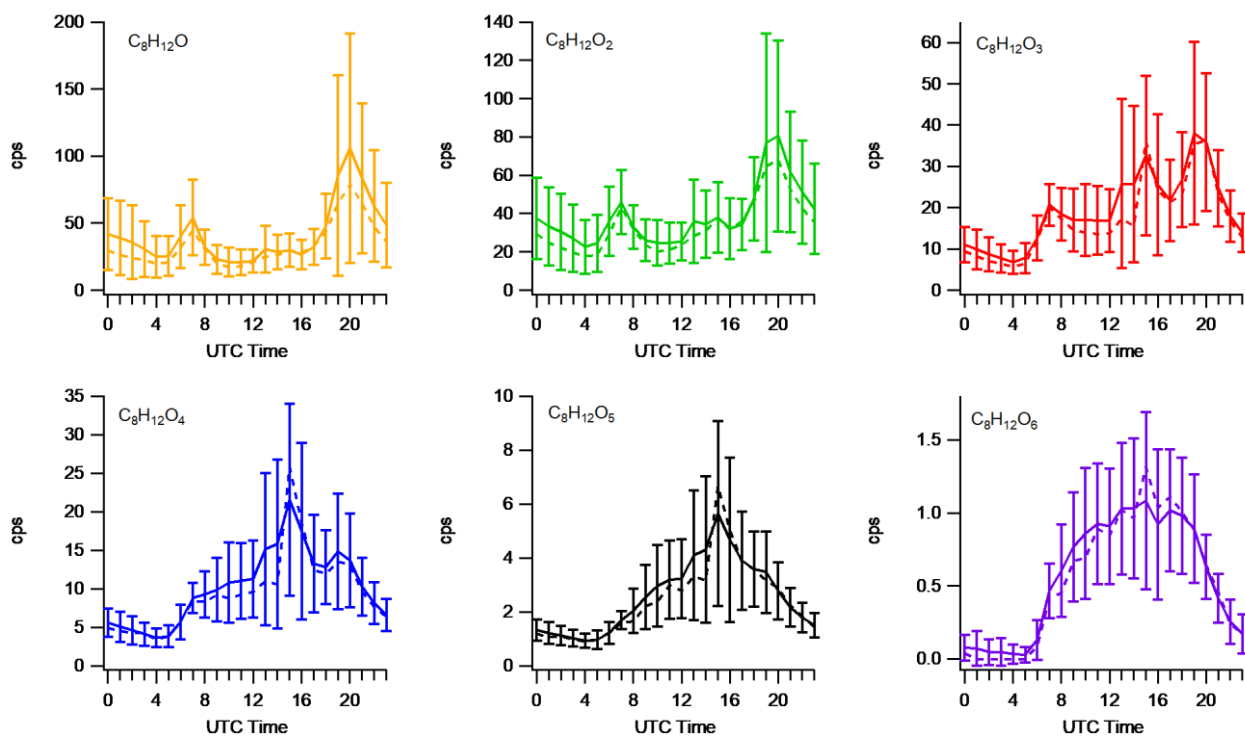


Figure S86. Diurnal patterns of non-nitrate monoterpene oxidation products: (a) $C_8H_{12}O$, (b) $C_8H_{12}O_2$, (c) $C_8H_{12}O_3$, (d) $C_8H_{12}O_4$, (e) $C_8H_{12}O_5$, and (f) $C_8H_{12}O_6$.

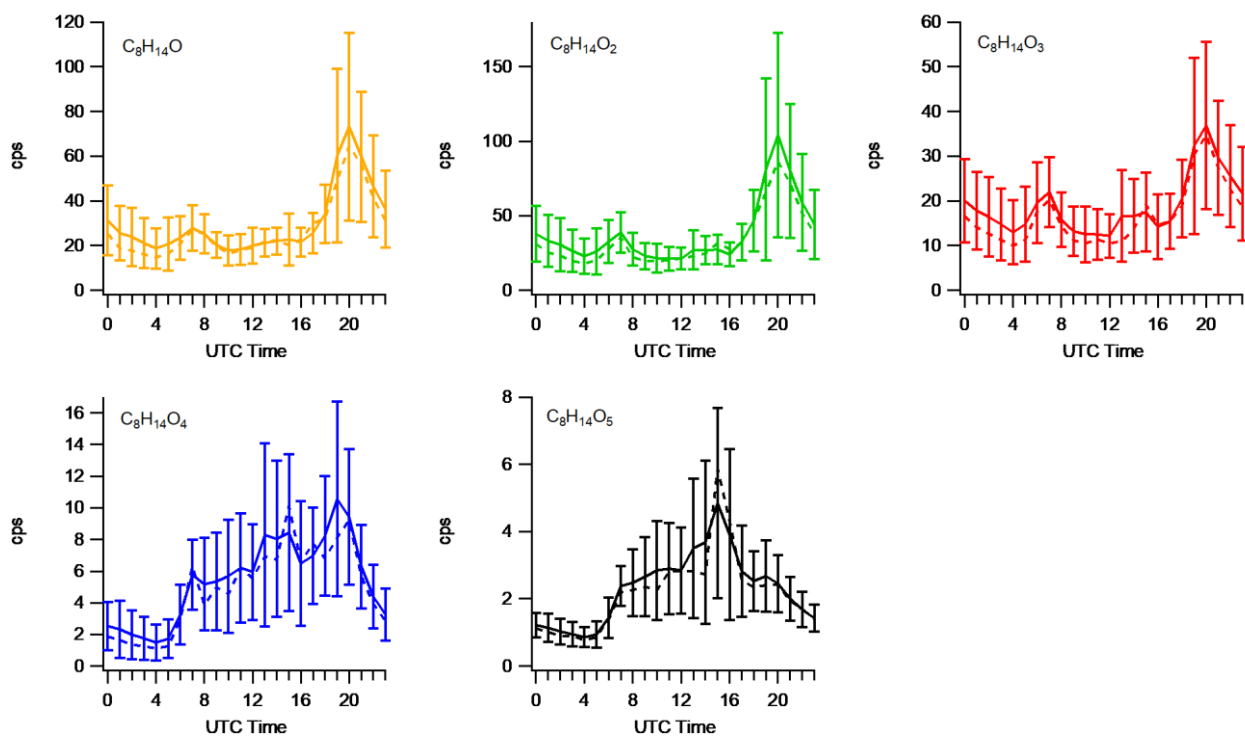


Figure S97. Diurnal patterns of non-nitrate monoterpene oxidation products: (a) $C_8H_{14}O$, (b) $C_8H_{14}O_2$, (c) $C_8H_{14}O_3$, (d) $C_8H_{14}O_4$, and (e) $C_8H_{14}O_5$.

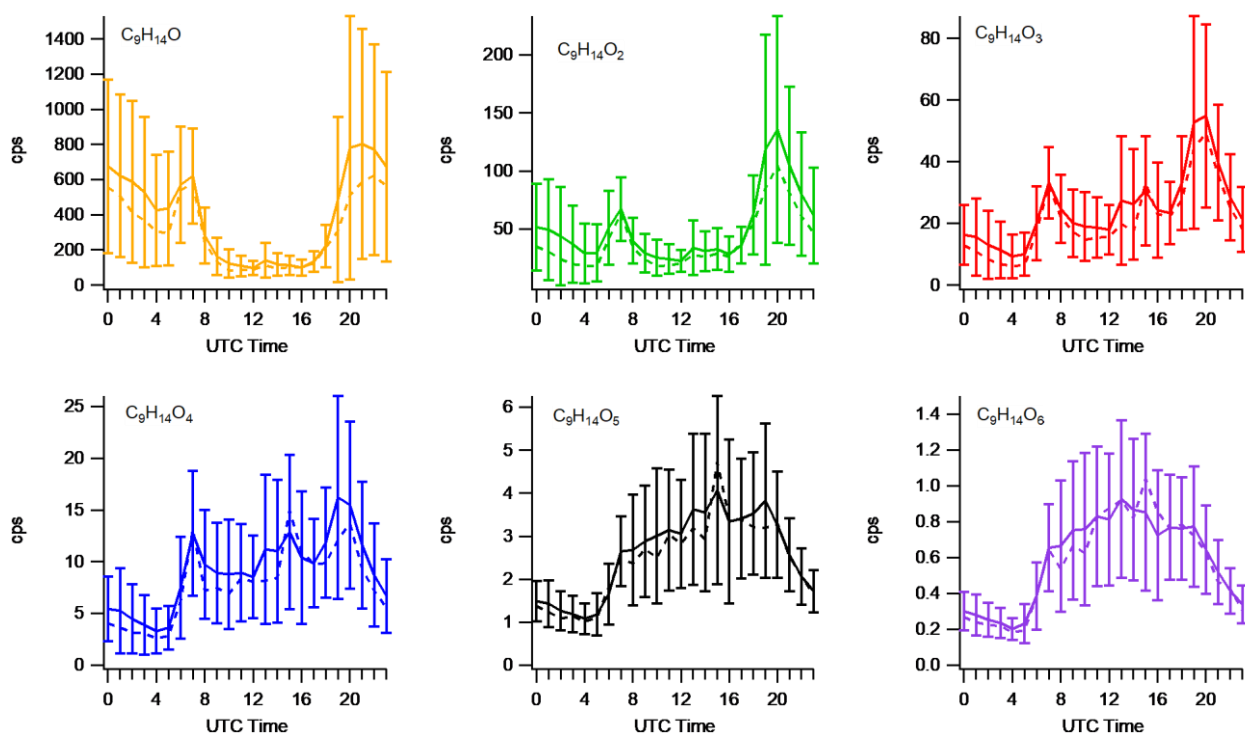


Figure S108. Diurnal patterns of non-nitrate monoterpene oxidation products: (a) $C_9H_{14}O$, (b) $C_9H_{14}O_2$, (c) $C_9H_{14}O_3$, (d) $C_9H_{14}O_4$, (e) $C_9H_{14}O_5$, and (f) $C_9H_{14}O_6$.

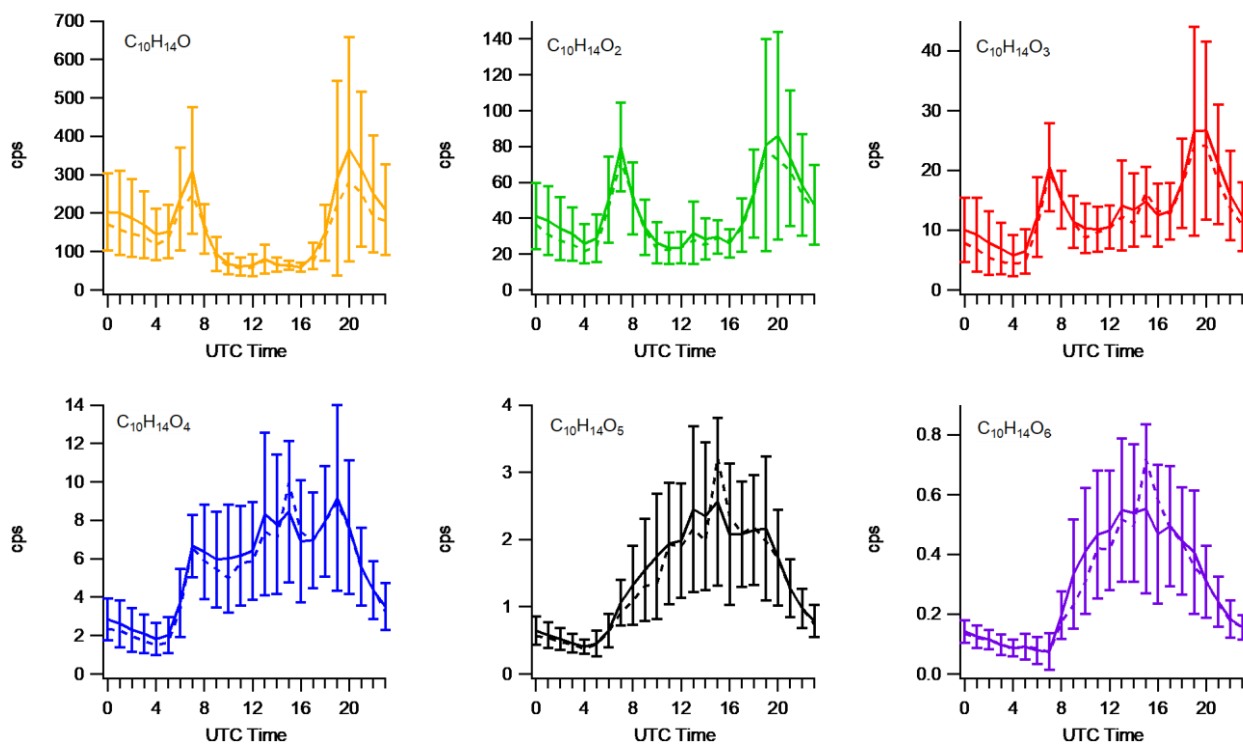


Figure S119. Diurnal patterns of non-nitrate monoterpene oxidation products: (a) $C_{10}H_{14}O$, (b) $C_{10}H_{14}O_2$, (c) $C_{10}H_{14}O_3$, (d) $C_{10}H_{14}O_4$, (e) $C_{10}H_{14}O_5$, and (f) $C_{10}H_{14}O_6$.

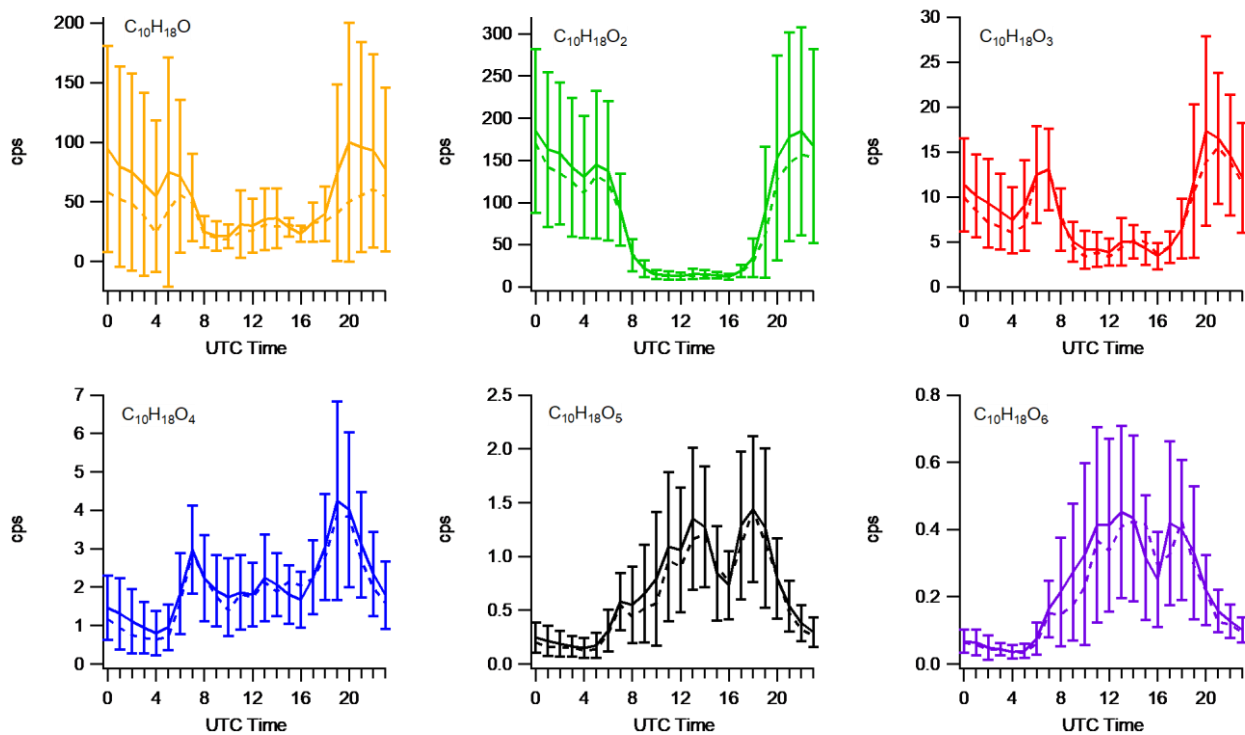


Figure S129. Diurnal patterns of non-nitrate monoterpene oxidation products: (a) $C_{10}H_{18}O$, (b) $C_{10}H_{18}O_2$, (c) $C_{10}H_{18}O_3$, (d) $C_{10}H_{18}O_4$, (e) $C_{10}H_{18}O_5$, and (f) $C_{10}H_{18}O_6$.

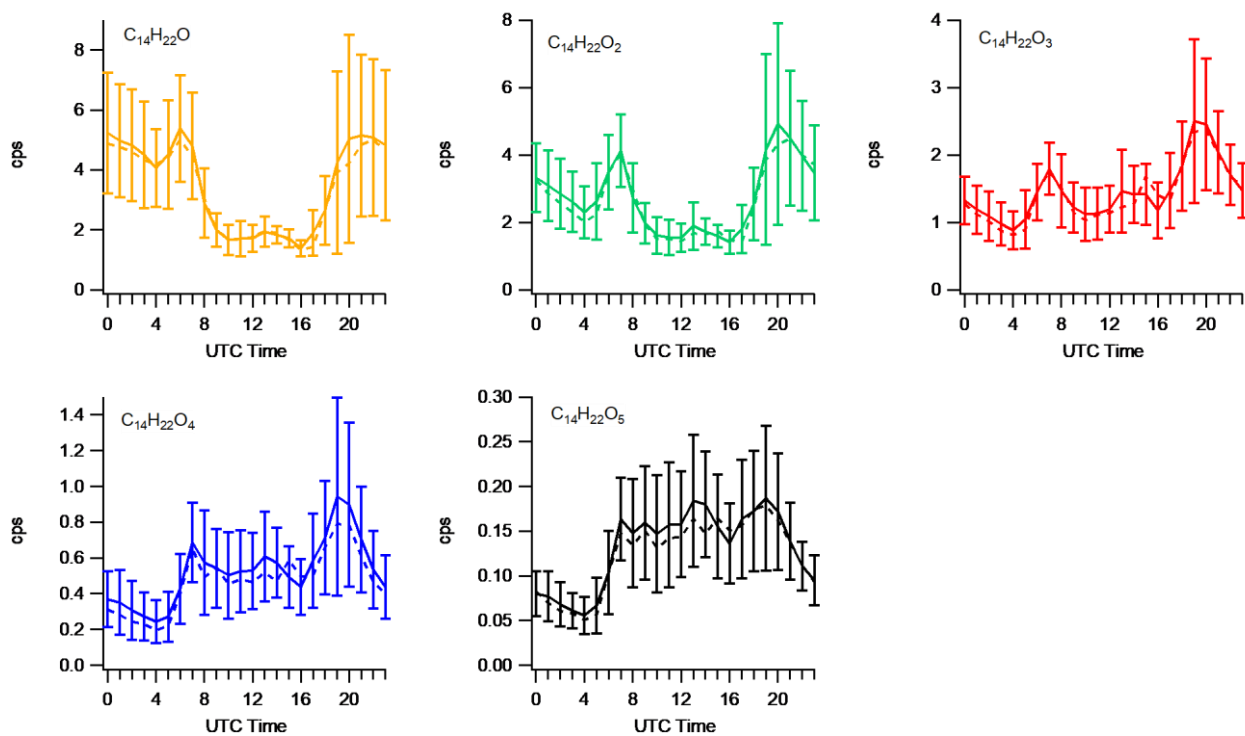


Figure S134. Diurnal patterns of non-nitrate sesquiterpene oxidation products: (a) $C_{14}H_{22}O$, (b) $C_{14}H_{22}O_2$, (c) $C_{14}H_{22}O_3$, (d) $C_{14}H_{22}O_4$, and (e) $C_{14}H_{22}O_5$.

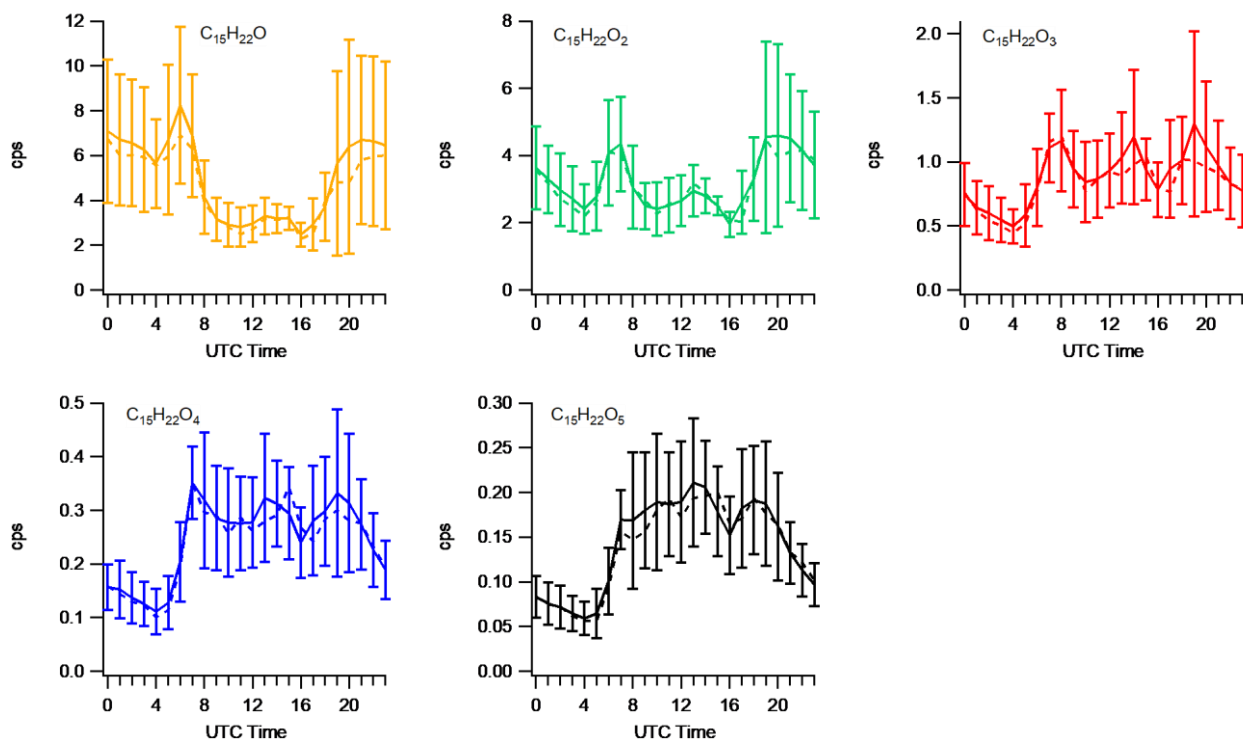


Figure S142. Diurnal patterns of non-nitrate sesquiterpene oxidation products: (a) $C_{15}H_{22}O$, (b) $C_{15}H_{22}O_2$, (c) $C_{15}H_{22}O_3$, (d) $C_{15}H_{22}O_4$, and (e) $C_{15}H_{22}O_5$.

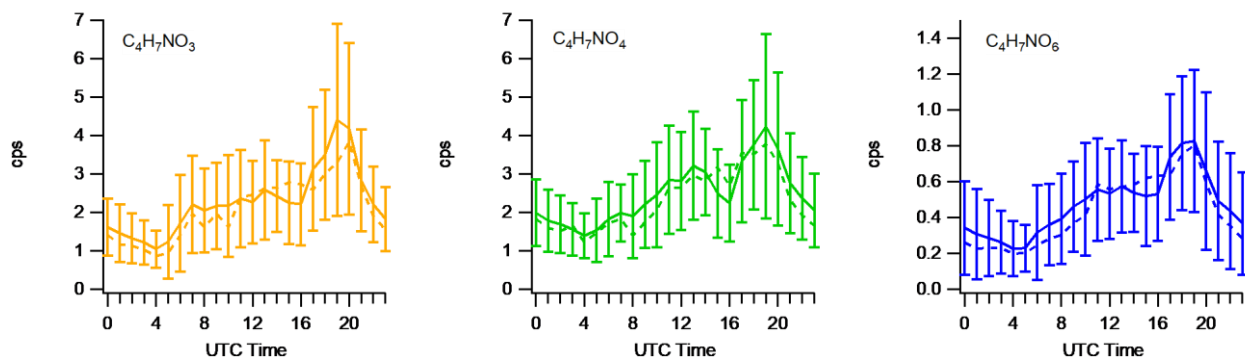


Figure S153. Diurnal patterns of isoprene-derived organic nitrates: (a) $C_4H_7NO_3$, (b) $C_4H_7NO_4$, and (c) $C_4H_7NO_6$.

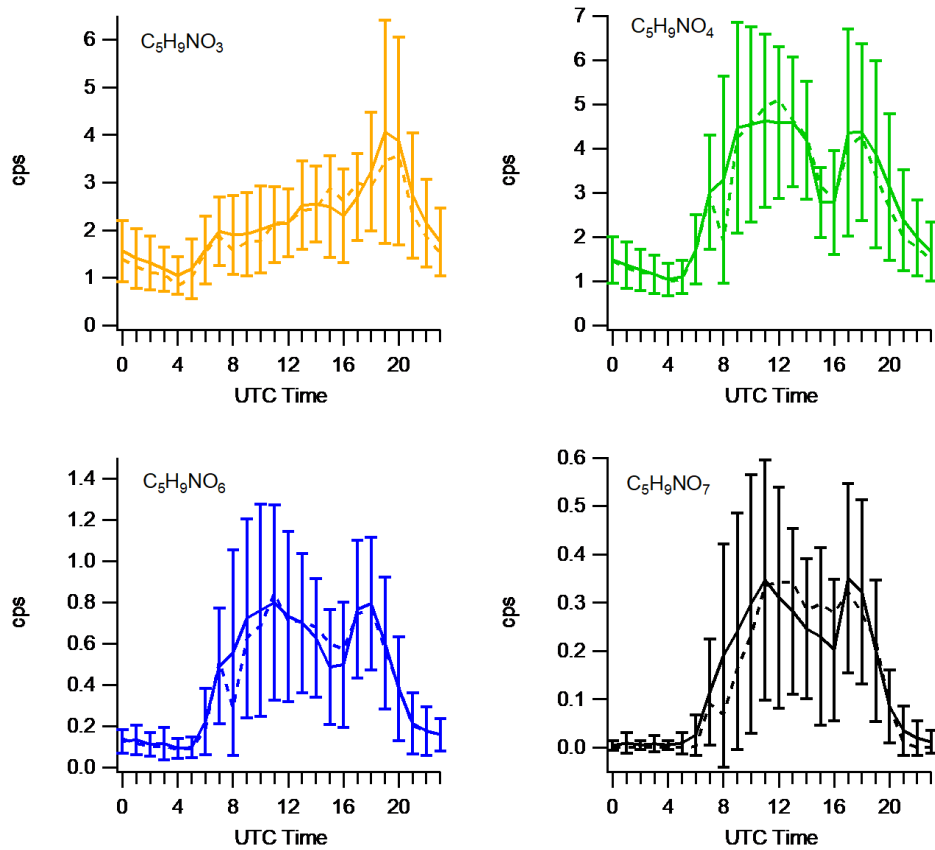


Figure S164. Diurnal patterns of isoprene-derived organic nitrates: (a) $C_5H_9NO_3$, (b) $C_5H_9NO_4$, (c) $C_5H_9NO_6$, and (d) $C_5H_9NO_7$.

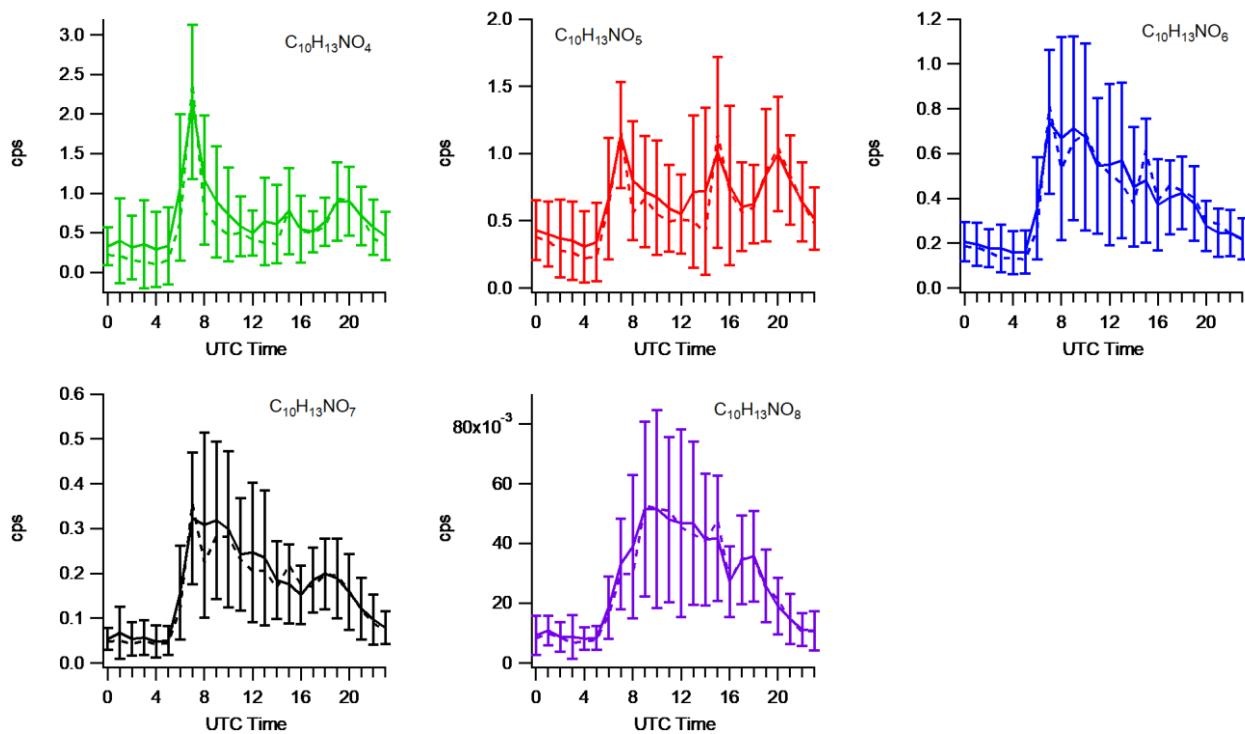


Figure S175. Diurnal patterns of monoterpene-derived organic nitrates: (a) $C_{10}H_{13}NO_4$, (b) $C_{10}H_{13}NO_5$, (c) $C_{10}H_{13}NO_6$, (d) $C_{10}H_{13}NO_7$, and (e) $C_{10}H_{13}NO_8$.

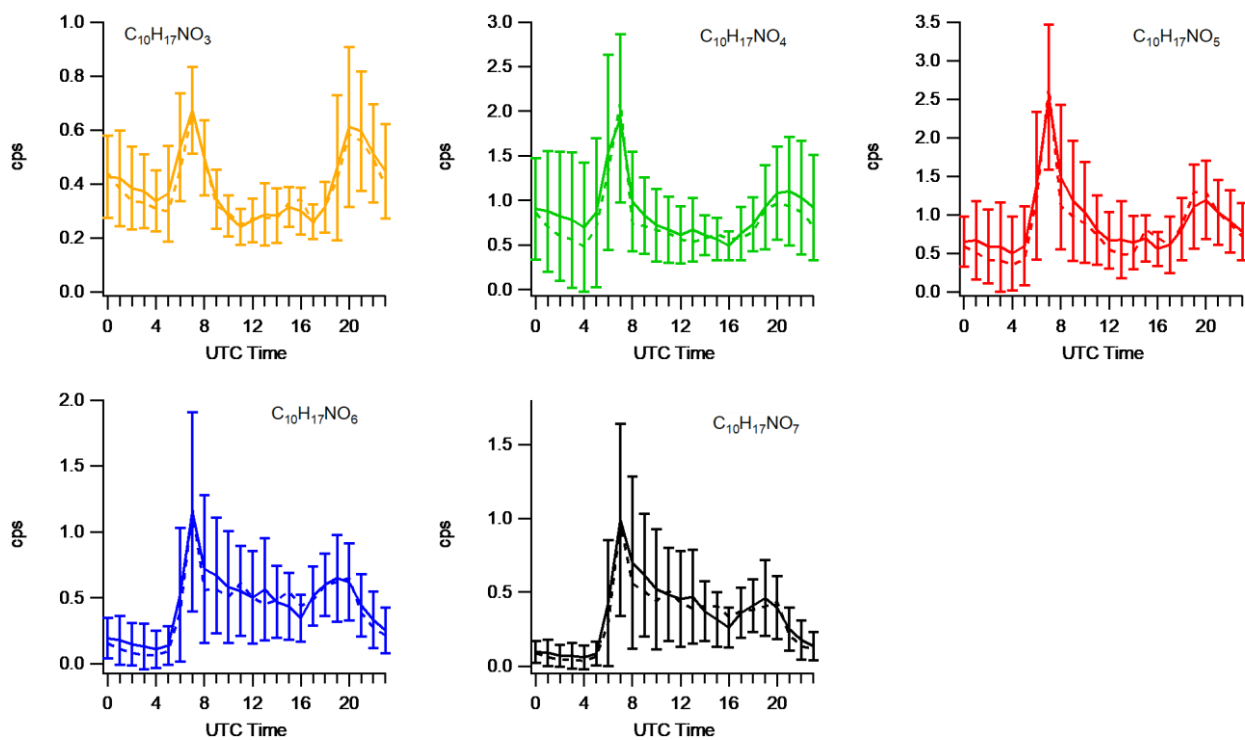


Figure S186. Diurnal patterns of monoterpene-derived organic nitrates: (a) $C_{10}H_{17}NO_3$, (b) $C_{10}H_{17}NO_4$, (c) $C_{10}H_{17}NO_5$, (d) $C_{10}H_{17}NO_6$, and (e) $C_{10}H_{17}NO_7$.

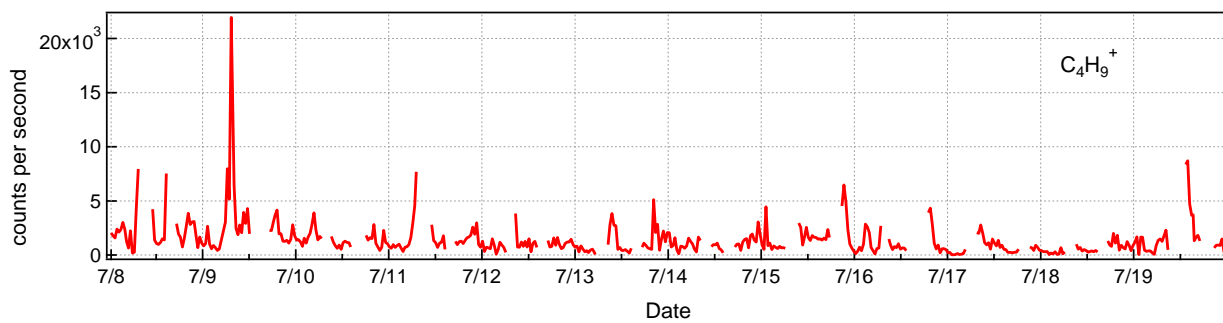


Figure S19. Time series of the identified $C_4H_9^+$.