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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Terpenes and their oxidation products in the French Landes forest: insight from Vocus PTR-TOF measurements" *by* Haiyan Li et al.

Anonymous Referee #2

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Review of Li et al.

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.

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. $C_{11}H_{18}$, $C_{16}H_{26}$), benzenoids and secondary metabolites, well known in chemical ecology.

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).

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 metaloorganic 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 H_2S, $ClNH_2$?

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

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

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.

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

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

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

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

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?

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.

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.

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.

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

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 O2+ 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 H3O+ ions? Apart from the C4H9+ ion, one would also expect C3H7+ and C5H11+ ions from the O2+ chemistry. In any case, it is distracting to focus on the C4H9+ 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.

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.

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.

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.

Technical

C20) L61 “in” should be “of”

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