

Answers to anonymous referee #2

Gkatzelis and coworkers report measurements of gas-to-particle partitioning of products from biogenic oxidation using three recently developed aerosol inlets and parallel gas-phase measurement. They developed an approach for identifying fragments in data due to thermal dissociation and ionic dissociation. The authors did a decent job in discussing C* intercomparison of 3 aerosol sampling systems and comparison of measured volatility to theoretical calculations. This PTR-based technique can be implemented to promote research in this area. The paper is generally well written. It has a heavy focus on techniques and how they affect the results. I understand that more details are in the cited Gkatzelis (2017) and some are discussed later in the Results section. However, I feel the authors should provide a little more information when relevant and/or refer to the specific section that you discussed in more detail (see specific comments).

We thank the Reviewer for all the comments. We increased the clarity by adding information regarding the measurement techniques and how the differences between the instruments might and can influence the results. For details please see our answers below and also answers to Reviewer 1.

Specific comments:

Line 82: Should be “known”.

Answer: Corrected.

Line 86: Where does the 10-40% come from? Please cite relevant references.

Answer: Please see answer to a similar comment of Reviewer 1.

Line 173: Why ACM and TD have different final temperature? How does this affect the compounds they measured?

Answer: Each instrument was operated during the measurement campaign using best practice by each of the respective groups to achieve optimal measurement results based on previous experience. One expected effect is that the ACM might not desorb and detect compounds which are in the additional temperature range covered by the TD. Therefore, the ACM might measure less compounds than the TD but this would have no influence on the results since we restrict the analysis to measured ions which we identify with our method as likely being parent ions.

Line 176-183: The PTRs were operated under different conditions. When you calculate C* using G/P ratio measured by different PTRs (e.g., TD for particle, a standalone PTR for gas), how did you treat the different sensitivities? In addition, a very simple schematic in SI, or table, showing all the instruments connected to the chamber might be helpful to readers, since the authors refer to the different operating conditions, inlets etc. frequently in discussion. Some time series examples of each technique in SI, along with Figure S1, will also be useful.

We included in the SI Table S2 which shows the details of the conditions for every PTR-ToF-MS used in this study. Difference in sensitivities of the two instruments did not affect this comparison but the main source of uncertainty was introduced due to the different E/N operating conditions. This is now discussed in more detail in the manuscript and has been the main focus of our previous publication (Gkatzelis et al., 2018). The following sentence is added in the manuscript and also the suggested

example time series in the SI in Figure S8. Figure S8 was also added at the end to these answers below.

“Finally, differences in sensitivity for each PTR-MS introduced minor deviations in this study and are discussed in detail in Gkatzelis et al., (2018). A characteristic timeseries of a major oxidation product from the β -pinene ozonolysis for the three different techniques can be found in Figure S8.”

Line 187: It sounds like the PTFE filter is always before the ACM-PTR-MS then how can the ACM collect particles?

Answer: The description of all instruments was significantly extended in the instrumental section of the manuscript. For all details please see answer to Reviewer 1. The fact that the ACM measures both, gas- and particle phase, was especially clarified. The relevant changes in the manuscript are as follows:

“The ACM has two sample air inlets. For the gas phase inlet air passes through a PTFE particle filter and is then directly introduced into the PTR-MS. For particle collection via the second sampling line air is passing through an aerodynamic lens removing gas phase and collimating particles onto a beam. The particles are subsequently passing a vacuum chamber and are collected on a cooled sampling surface. Once collection is finished particles are desorbed and transferred via a carrier gas (N₂) to the PTR-ToF-MS detector. Important to note is that during the collection process the PTR-ToF-MS is measuring the gas phase in parallel allowing for quasi simultaneous characterization of gas and particle phase.”

Line 252: Please be explicit what typical vaporization enthalpies are.

Answer: Added.

Line 253: A change of 15 C will result in C* change larger than 10 ug/m³. For example, a compound with a C*=100 ug/m³ at 290 K will have a C*=700 ug/m³ at 303 K. It is worth to consider and discuss this in the following comparison.

Answer: Please see the answer to Reviewer 1 for the same question.

Line 286: Can the authors estimate the uncertainty caused by operating gas and particle phase measurements under different ionic dissociation?

Answer: Ionic dissociation in the PTR-MS detector is compound dependent. Therefore, a general uncertainty cannot be estimated/applied to the different E/N conditions of the PTR detector. Due to the thermal desorption of the particle phase thermal fragmentation occurs additional to the ionic fragmentation for the particle composition measurements. Since it is not possible to distinguish thermal fragmentation from ionic fragmentation with our measurement techniques estimating uncertainties is not feasible.

Line 317: Did the authors do similar test for organic nitrate products (-HNO₃)?

Answer: Please see the answer to comment of previous reviewer regarding lines 307-309 in the manuscript.

Line 342: Should be “percentage”.

Answer: Corrected.

Line 354: Should be “previous”.

Answer: Corrected.

Figure 2: The error bar for the green dots need a darker color since it's hard to see. The ACM C*s don't have any error bar. Why, too small? In addition, since only averages were presented, it'd be worth to mention in section 2.4 that you calculated C* from equation 2 using how many samples for each technique for each experiment. As temperature varied though an experiment, how was C* affected?

Answer: Colors were changed for Figure 2. ACM had the lowest time resolution thus the number of data points was the lowest in comparison to the other instruments. This is the main reason why the error bars are lower for ACM in comparison to TD and CHARON. In Section 2.4 additional sentences were added:

“Calculation of the average C for every experiment was performed based on the time resolution of each instrument (section 2.2). When the signal in the particle-phase was close to the detection limit and introduced a high uncertainty, the calculation of the C* was not performed.”*

Figure S6: Temp = 280K, why inconsistent with 298K used for experimental measurement mentioned at line 256? The name for each theoretical calculation is not consistent with that in the text, e.g., nano vs. NN.

Answer: The Figure S7 (see also answer to Reviewer 1) was added in order to be consistent with the temperature and the text. Also, this Figure was used in comparison to S6 to determine additional uncertainties in the theoretical calculations use during the subsequent analysis. For further details please see also answers to Reviewer 1 about uncertainty in theoretical vapor pressure calculation.

References

Gkatzelis, G. I., Tillmann, R., Hohaus, T., Müller, M., Eichler, P., Xu, K. M., Schlag, P., Schmitt, S. H., Wegener, R., Kaminski, M., Holzinger, R., Wisthaler, A., and Kiendler-Scharr, A.: Comparison of three aerosol chemical characterization techniques utilizing ptr-tof-ms: A study on freshly formed and aged biogenic soa, *Atmos Meas Tech*, 11, 1481-1500, 10.5194/amt-11-1481-2018, 2018.

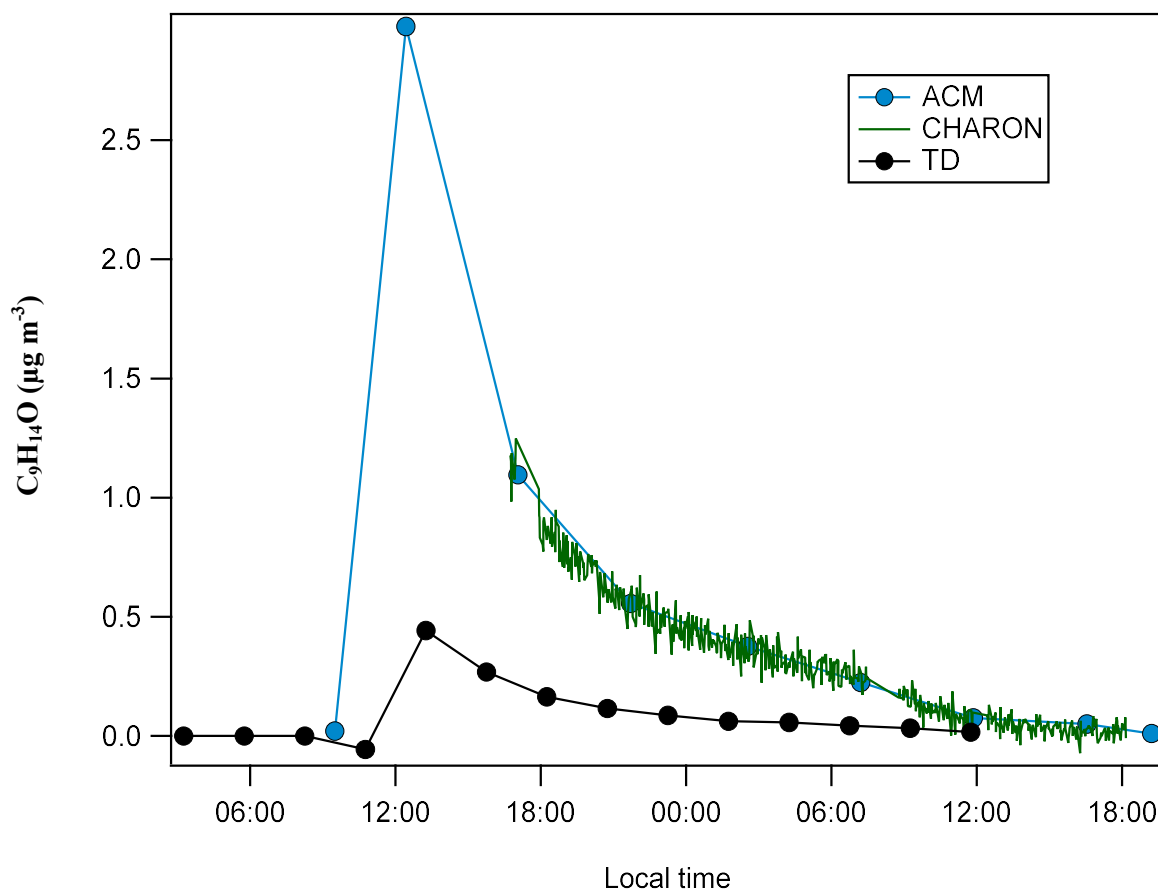


Figure S8: Characteristic example of the timeseries of $C_9H_{14}O$ for the three different inlet techniques