

## ***Interactive comment on “Gas-to-particle partitioning of major biogenic oxidation products from monoterpenes and real plant emissions” by Georgios I. Gkatzelis et al.***

### **Anonymous Referee #1**

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The authors present new direct measurements of the volatility of biogenic oxidation products, an active area of research in the field, using recently developed inlets for PTR-MS. The major foci of this work are the description of an approach for identifying fragments in PTR-MS data based on measured volatility, demonstration and intercomparison of 3 sampling systems for PTR-MS, and comparison of measured volatility to theoretical. The conclusions are well supported by the results and the recent literature, and the authors are clearly knowledgeable. The work is robust and valuable, and is in general presented clearly. The authors do a nice job of discussing some of the details and considering all of the possible sources of uncertainty. Though I think there are parts of the discussion and analysis that need to be refined and addressed, as indi-

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cated below, none are too scientifically substantial - only minor revisions are necessary for publication.

That said, my major concern is that I'm not completely convinced this publication is the proper journal, and wonder whether a more appropriate venue would be Atmospheric Measurement Techniques. Though some of the final conclusions and summary do get at scientific implications of the work, a substantial focus of the manuscript as currently written is devoted to developing an approach for identifying fragments in an instrument (Fig. 1), comparing between sampling approaches (Fig. 2), and demonstrating the capabilities of the approach (Fig. 3). Consequently, it reads somewhat more like it focuses on the techniques than the implications or results. I think it could go a bit either way, and leave it up to the editor, but would argue that it should perhaps go to AMT instead of ACP.

Major comments: 1. Throughout the discussion and presentation of this work, the authors seem to go back and forth somewhat on the lines between ions and molecules. At some points, the fact that the PTR-MS measures ions without structure is a major focus of the discussion. At others, figures and text seem to imply that this work is measuring one specific molecules. Often the authors later clarify, but it makes the discussion somewhat "blurry." As an example, the inset of Figure 4 strongly implies they are measuring nopinone, the fact that it is actually an ion with suggested by unknown structure is not discussed until 40 lines later and not mentioned in the figure. I recommend the authors state clearly when they are discussing ions they measured, vs. when they are discussing specific molecules, and generally shore up their language around these issues. It is a major point in comparing measured vs. theoretical volatility, which they acknowledge, but only really discuss near the end of the manuscript. I think a little reorganization would probably address the issue.

This also confuses the assumptions around fragmentation, since without structure their assumptions that loss of an e.g. C and O atom will increase volatility are not necessarily true (see below). I think their case could still be made, but it needs to be made a bit

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more carefully, and the fact that PTR measures ions, not structures is part of that discussion.

2. Comparisons between the ACM, TD, and CHARON are a major part of this work, but there is no real description of them. I recognize that the authors cite their previous work(s) for descriptions, but given the role of these comparisons in this work, at least some cursory description should be provided. How do they differ (other than temperatures and pressures)?

3. The authors often paint thermal and ionic fragmentation with one brush. In some ways that makes sense, I understand, but I don't think I fully agree they should be lumped. Thermal fragmentation is measurement of a molecules that was actually present in the particle as part of an accretion product. Ionic fragmentation is measurement of a molecule that was never in the ambient sample. In some cases this is a meaningful distinction. One major example is the decision to call VOCs fragments and exclude them from future analysis, yet IVOCs are included, even though they are almost certainly thermal fragments in many cases. Essentially the authors have decided that VOCs ( $C < 6$ ,  $O < 1$ ) are too small to be in the particle so are referred to as fragments, yet nopinone is included in the discussion, and later said to possibly come from thermal fragmentation. So then, what is the distinction between nopinone, which the authors continue to include, and those ions deemed "fragments" and excluded? Shouldn't VOCs thus be included in all the later analyses, and in the mass pie charts? They were, after all, observed in the particle phase. Or should those IVOCs be colored as fragments in Figure 1?

Also, the described approach to identifying fragments makes sense for ionic fragments, but not for thermal fragments, which may or many not have the same volatility as their parent (which may or may not be measured). Similarly, ionic fragmentation will likely have a relatively small impact on volatility, while thermal fragmentation probably has a substantial one. So this approach captures one pathway but not the other, suggesting discussion would be clearer if these two processes were more distinctly discussed.

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Overall, I think thermal and ionic fragmentation should not be treated together, for instance in Figure 1 and in discussion there and elsewhere (e.g. Section 3.1, lines 496, 593). They have different causes and different implications.

Minor comments: 4. There are significant grammatical errors and language quirks that belie the author as not a non-native English speaker. I have flagged many, but probably not all, below.

5. The introduction generally covers the topics, but it seems like often references are a bit out of place, missing, or not quite correct. I have tried to note these cases below.

Technical comments: line 47-48: "a detailed understanding...needs to be well defined" is odd English. Re-word.

line 54: missing comma between "pressures" and "thus"

line 76: "when applicable" can be deleted. Also, some of the cited works are indeed measuring ions, but others are measuring identified compounds, which is a potentially significant distinction as different molecules of the same formula may partition differently (as discussed latter). See Thompson et al. *Aerosol Sci. Tech.*, 2016, doi: 10.1080/02786826.2016.1254719. Also, citations should probably include Zhao et al., *ES&T*, 2013, doi: 10.1021/es304587x

line 79: For 2D-TAG, a more appropriate citation is probably Goldstein et al. *J. Chrom. A*, 2008, doi:10.1016/j.chroma.2007.09.094. I note that most TAG applications are not 2D, so it should be specific in the name here.

line 85: For SV-TAG, citation should include Zhao et al., *Aerosol Sci. Tech.*, 2013, doi: 10.1080/02786826.2012.747673

line 86: I don't disagree with the 10-40% estimate, but it should be cited.

line 95: Krechmer is one of many approaches to estimating  $c^*$ , and in fact is one of the more complex ones. I might also recommend citing Daumit et al., *Faraday Disc.*, doi:

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10.1039/c3fd00045a and Li et al., ACP, 2016, doi:10.5194/acp-16-3327-2016. Those two references directly parameterize by formula, which seems to be the reference in this sentence.

line 113: "Deviations...to" is a bit odd. Maybe "deviations between the theoretical and experimental"

line 130: should be "allows experiments to be conducted"

line 149: should be "extent"

line 168: Is it not a problem that the ACM is at sub-freezing temperatures? Does this not result in some gas-phase adsorption? I'm not sure because the description is sparse. Though the instruments are described elsewhere, given that this manuscript focuses in part on intercomparison, it would be helpful to include a few lines of description about each technique.

line 178: Why was the PTR operating differently for each collector? Could this have any impact, or is it calibrated for?

line 187: Do I correctly understand that all gas-phase measurements are thus passed through a filter? If so, I think this could substantially bias the measurements toward removal of gas-phase compounds and so higher measured particle partitioning. How was this checked or corrected for?

line 204: "pptV" here and elsewhere doesn't need to be capitalized

line 206: should read "additional"

line 220: if I'm not mistaken, this equation should use the molecular weight of the absorbing material, not the compound being absorbed. It looks like that is what is done, but is not what is stated in the description.

line 253: relationship between temperature of  $c^*$  is log-linear, so a deviation of 15 degrees should vary  $c^*$  by a multiplier, not a specific number (e.g. 10 times, not 10

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ug/m<sup>3</sup>)

line 253: I'm not completely convinced those temperature variations are as negligible as the authors seem to assume. Take for example the mixture experiment, with SOA concentrations of 60 ug/m<sup>3</sup>. A compound with a  $c^*$  of 60 ug/m<sup>3</sup> at 25 degrees (e.g. a triol with 7 or 8 carbons, based on SIMPOL) has a  $c^*$  of 10 ug/m<sup>3</sup> at 15 degrees, the range of temperatures in the experiment. That is the difference of 0.8 log units, and means that in the experiment it is the difference between half in the particle and 85% in the particle. Not a huge difference, perhaps, but enough to potentially be a source of uncertainty given the error bars on Figure 1, and probably worth exploring and discussing.

line 294-295: it is a bit confusing to say their volatility ranged from 1 to 4. Maybe just say "10<sup>-1</sup> to 10<sup>-4</sup> ug/m<sup>3</sup>"

lines 298-304: I agree that ions that small are likely fragments, but this does not mean that larger ions are not, so the cutoff to include above and disregard below feels a bit arbitrary. See general comments above.

lines 307-309: This assumption of functional groups decreasing volatility makes sense for pure components, but disregards potential impacts of structure. For example if the ion C<sub>8</sub>H<sub>12</sub>O<sub>2</sub> represents a dione, the ion C<sub>7</sub>H<sub>12</sub>O could be an alcohol so be held in a polar particle by stronger hydrogen bonding. I'm not totally convinced that without knowing structures the authors can definitively claim that 2 ions that differ by the atoms that could be a functional group will necessarily have a given relationship in volatility. Previous work (e.g. the Isaacman-VanWertz et al., 2017 reference cited in the manuscript) has used correlation of the timeseries of ions to assess potential overlap, could something similar not be included in this analysis to confirm that fragments covary in time as well as volatility? Also, how did the authors deal with nitrates, given that some of the ions contain nitrogen, is loss of the nitrate group possible and/or considered?

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line 333: "promoted" should be "supported"

line 359: "0.5 volatility resolution" sounds odd. Maybe add "bin" or units

line 381: missing "and"

line 406: the authors are referring here to the oxidation state of the carbon within the compounds, so should use OS\_C as the abbreviation

line 442: For tree emissions in Fig. S5, it looks to me like there is significant bias between the two approaches, not just random noise. Why might that be true for only this experiment? Does this imply anything for the other comparisons?

line 444: remove "existed"

line 461: misspelled "yielded"

lines 461-477: The detailed discussion of differences between vapor pressure estimation techniques do not seem necessary here. While it is a nice overview, it feels fairly tangential to the focus of the paper and could be removed or moved to the SI.

lines 478-479: In the initial discussion of Figure 4, and in Figure 4 itself, the authors seem to imply they are measuring e.g. "nopinone" not just an ion of the same formula. They go on to have a good discussion of this fact, but it should be made clear throughout the discussion and in the figure. (In other words, the inset of Figure 4 is not really an apples-to-apples comparison, which should be clear).

line 504: This approach to constraining the uncertainty due to structure is nice, but its description is a little unclear. "within the estimated uncertainty" of what - the experimental values, or the theoretical nopinone values?

line 529: misspelled "AIOMFAC"

line 534: particle phase is humidity dependent, these experiments are at 55%, which could sort of go either way, liquid or solid, for instance see Bateman et al., Nature Geo,

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2015, DOI: 10.1038/NGEO2599

Figure 2: Re-label as a-h, not 1a-2d.

Figure 3: I found sizing by oxygen number to be quite confusing. I recognize the utility of it in Figure 1, but in this figure that information is already more or less captured by the axes, and it serves to highlight certain ions for no real scientific reason. Sizing by concentration or not at all might be more appropriate here.

Figure 5: On some monitors, the dashed lines to isomers cannot be seen. Perhaps darken or color them.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-96>, 2018.

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