

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2022-279

Anonymous Referee #2

Referee comment on "Influence of ozone and humidity on PTR-MS and GC-MS VOC measurements with and without a Na₂S₂O₃ ozone scrubber" by Lisa Ernle et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-279-RC2>, 2022

Ernle et al. present an analysis that evaluates the role of ozone, and the impacts a understudied (and affordable) ozone scrubbing material, on VOC artifacts observed by PTR-MS and GC sampling. The authors first evaluate the role of ozone on producing artifacts in the absence and presence of VOCs, then evaluate the efficacy of implementing a Na₂S₂O₃ scrubber to remove ozone and limit inferred artifacts. The authors then characterize the scrubber determine important characteristics such as breakthrough, lifetime, and effects of humidity

Overall, the paper is well organized, easy to read, and the figures are easy to interpret. I agree with a number of the conclusions drawn by the authors regarding artifacts of aldehydes, but I have a number of concerns about the conclusions drawn from the observations of the alkenes. Specifically, I question whether these observations are an "artifact" – i.e., something artificially produced by the instrumentation and sampling setup - or a reflection of an ozonolysis experiment that is expected to occur when alkenes are mixed with ozone. My main comment (below) elaborates on this further, and I hope that the authors can dig deeper into the data to address this primary concern.

Main Comment:

My main comments pertain to the conclusions drawn from the various tests. What I haven't fully appreciated from the discussion is whether the tests really demonstrate an artifact, or simply shows that effect of VOC ozonolysis. To help frame my questions, I've listed the main takeaways I drew from the discussion and conclusions.

- In the presence of high ozone (but absence of VOCs), aldehyde and isoprene artifacts are observed due to ozone surface reactions with organics bound to Teflon tubing. Aldehydes are observed to increase in both the GC and PTR, while isoprene artifacts are observed by the PTR due to fragmentation of aldehydes.

- When steady mixing ratios of VOC standards are sampled by both instruments, the mixing of high ozone results in a positive aldehyde artifact. Part of this artifact results from surface reactions described in (1), while the remaining artifact may be due to reactions of VOCs with ozone in the tubing, instruments, or both.
- When steady mixing ratios of terpenes and sesquiterpenes are sampled by the instruments, the introduction of high ozone results in monoterpene and sesquiterpene decay for both instruments.
- The presence of the scrubber material removes ozone and limits decay of monoterpenes, but not sesquiterpenes.

I'm convinced that conclusion (1) is consistent with a sampling artifact, and I fully agree with the authors that this presents an important consideration when sampling in high ozone environments.

Conclusions (2) and (3) are drawn from an experimental setup that essentially simulates VOC ozonolysis, and point (4) simply shows that removing ozone prevents VOC oxidation. So, is this really an artifact, or just an ozonolysis experiment? What I would like to know is if there is additional chemistry in the tubing (or in the instruments) that is prevented by the presence of the scrubber? Or in other words, if I don't have a scrubber, and I were to measure terpenes in the atmosphere, would I measure a bias because of surface reactions? Right now, as described, it is not clear to me that that this is true and if a scrubber is needed for preventing these potential artifacts

I do think that the authors have the data to demonstrate whether these effects are present and perhaps can expand this discussion. For example, Fig. 3 seems to show that the GC has a higher positive bias than the PTR for acetaldehyde as the VOC mixture is increased at high ozone (i.e., the change in acetaldehyde from 50 – 1000 ppb is much higher for the GC than for the PTR). Is it possible that this is an artifact of the GC preconcentration? In such a case, I would agree that this is an instrument artifact. Are similar observations made for the monoterpenes and sesquiterpenes? I.e., are there relatively larger negative biases for the GC than for the PTR? Again, this would be convincing of a negative bias owing to instrument sampling and would warrant the use of an ozone scrubber to limit the sampling artifact.

Other comments:

Line 64: Are there studies which show the effects of new vs. old tubing on VOC measurements?

Line 90: A lot of experiments were performed under a range of different VOC conditions. I might suggest including a table that lists out experiment conditions for clarity to the reader.

Line 114: While fragmentation is less of an issue for many of the analytes, a number of these species (and their products) do fragment (e.g. siloxanes, monoterpenes, sesquiterpenes, etc), and can impact important measurements of species such as isoprene, as demonstrated by the authors. I suggest rephrasing and referencing relevant fragmentation papers (e.g. Pagonis et al).

Line 150 and Table 1: Could the authors propose a quantitative measure for each interference? For example, the increase in signal during zero VOC injection (e.g., amount of VOC signal produced per ppb of ozone introduced) would be helpful in quantifying positive artifacts owing to ozone interactions with the walls of the tubing and/or instrumentation.

Table 1: As mentioned in my main comment, I'm still not quite sure if what is presented for monoterpenes and sesquiterpenes is an interference per say, and so I would be hesitant to include a down arrow for these species without further digging into the data and demonstrating that the high ozone is leading to additional biases beyond those of an ozonolysis experiment.

Figure 2: This caption feels incomplete and really doesn't describe what the authors are trying to show. It may be better to say "Effect of ozone mixing ratios (0, 50, 1000 ppb) on GC and PTR-MS measurements of chlorobenzene under a range of VOC mixing ratios (X - X ppb)"

Lines 158 – 161: These sentences feel a bit distracting and I don't think are necessary for the discussion. This statement could be removed, or simply stated – e.g. "While the instruments observe slightly different mixing ratios owing to differences in sensitivity, the relative change in chlorobenzene mixing ratios remain unchanged when ozone is present."

Line 165 - 166: Can the authors expand here? What trends or aspects of the measurements agree with what was observed by Northway et al. and Lehmpuhl et al.?

Line 169 – 173: Here, the authors discuss the observations of acetaldehyde for each instrument independently. I'm also interested in the relative changes between the instruments. For example, it seems that the GC observes a significantly higher change in acetaldehyde at high O₃ than the PTR. Is this due to a longer inlet line, differences in the residence time, or possibly differences in the instruments that that are causing these effects (e.g., ozone in the GC trap)? At first glance, this looks like this could be a combination of line impacts and instrument artifact for GC, while for the PTR this looks

more like an effect of aldehydes production from the surface reactions of the tubing since the changes in the presence of ozone at the various VOC mixing ratios seem to match the changes in signal when VOCs are absent (as demonstrated in figure 4b).

Line 178: Do the GC signals sum up to what is observed by the PTR?

Figure 10: Is this measurement by PTR or GC? Please specify in the caption.

Line 330: I presume humidity didn't have a strong effect on the oxygenates or other species that had a positive artifact during ozonolysis?

Line 360: Citation for the stratospheric observations? Also, It would be helpful to compare these interferences to those observed in the stratospheric work to put into perspective the real-world implications of these interferences.

Technical Comments:

Line 27: Suggest "measured" in place of "covered"

Line 31: Suggest "mixing ratios" in place of "values"

Line 62: It would be more helpful to point to Table 1 as opposed to Section 3 for the list of VOCs.

Line 64: Suggest "instrument" or "technique" in place of "machine"

Line 95: Suggest "instruments" rather than "mass spectrometers" since the GC is not solely a mass spectrometer

Line 186: "Netto" should be "net"

Line 190: The wording is confusing - perhaps "compounds with positive artifacts"

Line 261: Suggest "junction" in place of "T-piece"