

Review of "Influence of ozone and humidity on PTR-MS and GC-MS VOC measurements with and without Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> ozone scrubber by Ernle et al., <https://doi.org/10.5194/amt-2022-279>

The manuscript tackles an imported artefact associated with in-situ VOCs measurements, especially in polluted (ozone-rich) environments on ground-based sites and the upper troposphere and lower stratosphere. The paper is well structured and focused and a pleasure to read. Congratulations!

Still I have a couple of issues that need to be clarified (see minor concerns) and one general comment.

**General comment:**

By integrating the ozone scrubber just before the two instruments, the observed artefacts are basically gone. This implies that the ozone-driven chemistry occurs within the instruments, namely in their instrument inlet sampling system and the detection system. Both sampling and detection systems will differ quite substantially and to my understanding, the observed effects/artefacts often differ in their magnitude. It would be very helpful for all research groups using the two measurement techniques in the field, if you add a section "lessons learned" (or so) that summarizes your understanding of the problem and that lists your recommendations. I guess you will have learned a lot with the two different instruments and that you can give more advice than "just": install a sodium thiosulfate ozone scrubber. For instance:

- 1) Do you only expect surface effects (incl. memory effects) on the walls of the sampling system or may also gas-phase reactions (e.g. in the drift tube) play a role? Can these effects be minimized by using special sampling lines, e.g. made of PEEK or (silanated) silcosteel that show much smaller permeation and thus memory effects than lines made of PFA or FEP?
- 2) Another issue in this respect: All relevant reactions and their magnitude will depend on the cleanness of the instrument. Based on your experiences, can you give relevant advice, e.g. to clean the instrument before starting measurements with 500 ppb ozone for half a day? By how much the ozone-driven artefacts will decrease. Or in other words, with an uncleaned instrument, one can't get reliable data for some target gases such as acetaldehyde or acetone even at lower ozone m.r.? I also ask here because you haven't specified the pre-treatment of your instruments (you should add this, yet). And on L. 178/179 you write that just adding ozone increases the signal of the C<sub>3</sub> and C<sub>4</sub> carbonyls, most likely (but not written there) because of reaction of ozone with species attached/adsorbed at the walls of the instrument sampling systems.
- 3) Is the installation of such a scrubber accompanied with any disadvantages, e.g. the affection of certain species or an increased response time (due to memory effects)? If you don't have relevant experiences, you could speculate a bit, e.g. that (based on your understanding) such effects are unlikely or possible for certain species.
- 4) The effects occur between the location where ozone is added or present and somewhere in the detection chamber/system. During atmospheric measurements the reaction times are usually longer, as ozone enters the sampling line together with the

sample air and then travel in common until the detection system. Please estimate the total reaction (travel) time in your laboratory system so that other instrument users can judge the problem in their configuration.

### Minor concerns

- General remark: I suggest to use the term “zero air” instead of “background air”. The latter usually characterizes “not polluted” sample air. Moreover, is your synthetic air really clean or VOC-free, so that its influence on your experiments and results can be excluded?
- L. 73. Please add that ozone (as non-polar) molecule is little affected / solved in the water bubbler
- L. 78. Please use SI units, that is “hPa” instead of “mbar”.
- L. 80. How H<sub>2</sub>O and RH was measured and where? What is your reference temperature for calculating RH, just the laboratory temperature and you assume that the temperature of the scrubber assembly is identical?
- L. 111f (sections 2.2.2 and 2.2.3). Shortly describe the material (FEP, PFA, PEEK, silcosteel,...) and parts (sampling tubes, ...) that are in contact with the sample air and on which surface reaction can occur. And what are the residence (reaction) times in your system? See also general comments.
- L. 112. “hPa”
- L. 117. “was” before 2.85 m
- L. 131f. A major topic of your paper is the influence of the ozone scrubber. To better understand its functioning, you should add more information in this section. Do you use a filter holder with an inner diameter of 37 mm (or less)? What is the air residence time in it? Is the scrubber just a “tissue filter” (prepared as you described) or more?
- L. 164f, Fig. 3. Why the enhancements for the GC and the PTRMS are so different?
- L. 168/169. You write “This indicates that the interference is not instrument specific but more likely function of the common inlet tubing exposure to ozone.”. However, independent on the filament problem of the GC (that is at 2 ppb), the enhancement between 7:00 and 8:00 (and 1000 ppb ozone) is a factor of ~3.5 higher for the GC. I would conclude that’s not only an inlet tube effect or do you expect higher influences by the inlet sampling inside the GC. Please better explain this difference.
- Fig. 4a. What is the reason of the missing signal drop of the MGC at ~3:30 (and the moderate drop of the PTR), when the cal (acetaldehyde) signal jumped to 0? As both signals directly turn to 0 when ozone is switched off, this appears like a reaction of ozone at the surfaces of the sampling lines. Would this also explain the last point, namely the different behavior of both instruments?
- L. 176: “have the same exact mass” → “have exactly the same mass”
- L. 178/179. a) what is the process for the signal increase if ozone is added to zero-air and b) does this process/effect explain the two issues further up?
- Fig. 6. For what species “cal” stands for? ... 0.5 ppb propanal and 0.5 ppb acetone, that is, in sum 1 ppb? Then both instruments would measure too little (Fig. 6a and the MGC for C<sub>4</sub>) or too high (PTRMS for C<sub>4</sub>). Please better explain this.
- L. 183. “Propanal and butanal mixing ratios decrease under the same O<sub>3</sub> conditions ...” not so clear in my opinion, because the m.r. appears to increase later in the time series. I would describe this with “indifferent with a tendency to depleted m.r. or so”.

- L. 190. "It shows that exposure of the inlet tubing to high ozone does not rapidly clean the lines of the artifact inducing compounds." That's an important sentence and I guess the first time where you describe what's going on. I suggest that you add a further short section 2.5 having a title like "Potential effects causing ..." and a short description of a) surface reaction in the sampling lines, b) gas phase reactions in the sampling lines, c) gas phase reaction in the PTR detection system (e.g. in the drift tube or ??) and give them a real process name. Later in following sections you can refer to these three (or more?) "artefact reactions" and (if possible) detail the process further.
- L. 215-217. This part I haven't understood fully. What you mean with "in the very beginning"? After using a new FEP line, after switching to a new air matrix, after ...? And what you mean with "independent absorption"? Independent on what?
- L. 217-222. In my opinion, the text starting with "Note that ..." fits better in the experimental section.
- L. 227f (and Fig. 8). You say that the carbonyl compounds offset the expected signal drop with ozone or do you believe that the PTR doesn't show a depletion of the isoprene signal (in contrast to the GC) and you "only" see the positive offset from the carbonyl compounds? Please specify and clarify.
- L. 248f (discussion of Fig. 10). Sorry, I can't follow your explanations. First, I couldn't figure out in Fig. 10 when or during which periods the scrubber is connected and when bypassed. Please add bars (or so) at the top. Furthermore, between ~5:00 and ~7:20 at 2 ppb the sesquiterpenes never reaches the target concentration of 2 ppb, neither with nor without scrubber. I understand that this is due to the absorption/desorption (memory) effects. Still, it's hard to catch your main messages. It's a) that the scrubber has no influence (besides scrubbing ozone) and b) that the sesquiterpenes are strongly affected by memory effects? Is the memory effect limited to the sesquiterpenes and all other species just work fine and are not affected by the ozone scrubber? Please improve your explanations. For a better understanding, it would help a lot adding times or time periods.
- L. 270. "Scrubber endurance" would be a more suited title.
- L. 287-290. These details on the filter assembly belong to section 2.3. I understand that your filter assembly has not been perfect, as you inserted the scrubber tissue into the existing somewhat larger Teflon filter, correct? Can you add here in this section or maybe better in the "lessons learned section" (see general comments) if – based on your experiences – the scrubber/filter assembly can be improved, e.g. by using a suitable filter housing (avoiding bypassing) and more important by adding more scrubber tissues? This will increase the scrubbing efficiency and the scrubber endurance (correct and do you expect a linear scaling with the number of scrubber tissues?), but do you also expect negative effects?
- L. 346f. Only now/here (as you give a time period) I understand the cycle in Fig. 10. In Fig 15b, at 1:00 you switch to O<sub>3</sub>=50ppb and let this level until 2:00, but at 1:30 you add the scrubber and the measured O<sub>3</sub> signal switch to 0, although the O<sub>3</sub> level (by the O<sub>3</sub> generator) still is at 50 ppb, correct? As requested before, please indicate this cycling in the relevant Figs better.