

Atmos. Meas. Tech. Discuss., referee comment RC1  
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## Comment on amt-2021-354

Anonymous Referee #1

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Referee comment on "Ozone reactivity measurement of biogenic volatile organic compound emissions" by Detlev Helmig et al., Atmos. Meas. Tech. Discuss.,  
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The manuscript "Ozone Reactivity Measurement of Biogenic Volatile Organic Compound Emissions" by Helmig et al. presents a prototype instrument for the direct measurement of total ozone reactivity. This type of instrument has been proposed before, but the authors describe a different design with potentially better performance. Although the subject of the manuscript is clearly within the scope of AMT, I find that there is a general lack of details and information. Several of the experiments are not well described, and in many cases the reader is left to interpret the figures and diagrams to understand what was done and why. Moreover, there are several inconsistencies and errors in the text (e.g. about the residence time in the reactor and the calculation of the ozone reactivity) and some statements are not supported by the data as presented. A model is mentioned at various points, but is never described (not even with a reference to another publication). I would recommend that the authors thoroughly revise the manuscript and resubmit it.

### MAIN COMMENTS

The Introduction and Methods sections are very long. I would consider dividing them into subsections so that the material is organized better and easier to read. Two instruments appear to be described (one from CU and the other from Finland), but it is not clear whether they are identical (or what are their differences) and how they were used/deployed during this work. I assume not all the experiments described in the paper were done with both instruments at the same time. Ambient measurements in Finland are mentioned at various places in the manuscript, but the only data shown appear to be from Michigan (USA).

I am puzzled by the mathematical treatment of the ozone reactivity. Approximating the calculation of  $R(O_3)$  using a Taylor series (Supplement A) seems completely unnecessary to me, given that the rate equation has a very simple analytical solution. More importantly, throughout the text the authors report ozone reactivity in terms of  $\Delta(O_3)$ ,

which is not correct.  $\Delta(O_3)$  is the difference between the ozone measured before and after the reactor, from which ozone reactivity (which is in  $s^{-1}$ ) can be calculated. It is not just a matter of using the wrong unit, it can also cause incorrect results since reactivity depends on the ratio not on the difference of the two ozone measurements, as the authors themselves show with equation S5.

A few comments on the technical side of the instrument.

1) I don't quite understand what is the advantage of using four flasks as a reactor (as opposed to a linear reactor used by other studies). I get it that it makes the system compact and portable, but is there any other advantage with respect, for example, to the mixing of the sample with the ozone reactant or with the residence time? Why four flask instead of 2 or 6 with equivalent total volume? The design choices of the instrument should be explained, especially if it is claimed that they lead to improvements over other similar instruments.

2) From figure 3, it seems that ozone is added to the sample before the mixer and then the flow of ozone+sample is split before it enters the 4-flasks reactor. Surely this introduces an error in the determination of ozone reactivity, as BVOC start reacting with ozone in the mixer and the measured "O<sub>3</sub> before the reactor" results lower than it actually is. This of course depends on the residence time in the mixer and along the lines that connect it to the reactor, so it may be negligible, but the authors should address this potential issue.

3) It is repeatedly stated that the reactor flow in the default configuration is 5 slpm. However, from figures 3 and 5, it looks like the actual flow is 4.4 slpm (4.5 sample + 0.5 ozone - 0.6 to the monitor). On page 22, the reactor flow is declared to be 3.6 slpm. What is the actual reactor flow? If different flows were used for different experiments/measurements, it should be clearly stated and it should be explained why it was necessary to do so.

4) I think that the discussion of the detection limit (page 13) is misleading. The sensitivity of TORM is not "slightly higher" than the sensitivity of the Matsumoto (2014) instrument: the difference is about a factor of 2, similar to the difference with the Sommariva et al (2020) instrument. In any case, the actual detection limit of the TORM instrument is of the order of  $1e-4 s^{-1}$  (page 22), which is higher than both the Matsumoto (2014) and the Sommariva (2020) instruments.

5) After pressure balancing, the authors indicate that the ozone measurement artifact is about 1.7 ppb. Were the data corrected for this artifact? Is the artifact dependent on any ambient parameters (pressure, temperature, humidity)? Why does figure 5B shows 2 valves and figure 5A shows only 1? It would also be good to know whether the valve added to control the pressure can cause any significant loss of ozone.

Section 3.3. Why was it necessary to normalize the reactivity measurements to the air flow and the weight of the branch? A reference to Supplements C and D, and a basic description of the experimental setup for these experiments is missing from the text. It is also not clear what the "blank experiment" was: supplement D mentions a "soil chamber enclosure", which seems to suggest a different type of chamber than the one used for the branch enclosure experiments, but there is not enough explanation. The points and lines in figure 6B are very hard to see and the y-axis labels in figures 6A and 6C are not clear (what is "API" that is subtracted from the 49C measurements?). It would also appear that the  $\Delta(O_3)$  from an empty chamber (figure 6B) is often higher than the measured  $\Delta(O_3)$  (figure 6A) but I guess that cannot be the case, so some explanation should be added to the text. Was the reactivity measured in the empty chamber subtracted from the reactivity measured in the full chamber?

Section 3.4. What is the purpose of changing the plumbing of the reactor? It only shows that in the changed configuration the residence time is a little longer. In any case, why was the residence time determined using a 4 slpm flow, when the actual reactor flow is 4.4 (or 5, see comment above)? In the end, the authors settle on a 120 seconds residence time, which suggests that the theoretical value calculated at 5 slpm was used. But this does not make sense as the experiment described in this section indicate that the theoretical value is ~30 seconds too long compared to the actual value. In addition a residence time of 167 seconds is mentioned on page 22 and a value of 150 seconds is used in Supplement B. The residence time is a key parameter of the system, and therefore it should be clear what it is. The work in this section should be better explained and the reasoning behind the choice of the final value used for all subsequent analysis should be clearly explained.

Section 3.5. The authors refer to previous studies and earlier experiments on the effect of humidity on ozone measurements: the appropriate references are missing. At line 730, the authors say that an interference can be caused by the addition of water to the sampling flow. It is hard to judge this statement without information on how much water was added, and whether it is comparable to ambient levels and/or to the levels in the enclosures. It is also not clear what is meant with the statement "The bias in the ozone recording lasted significantly longer (10 times) then the residence time". Was the interference significantly larger than the inherent variability of the ozone source? There is not enough detail on these experiments and their description is not clear. I also assume that the reactivity data were corrected for the residual water interference on ozone: supplement G clearly shows that the combination of a Nafion dryer with a differential monitor reduces but does not eliminate the interference, so it is misleading to state that this setup eliminates the need for correction algorithms (lines 691-692).

Section 3.6 (laboratory test). I do not understand the point of this section. Figure 9 shows that the theoretical reactivity based on the assumed concentration of limonene is linearly correlated with the measured and modelled reactivity. There are several problems with this: first, the authors do not know exactly the concentrations of limonene being measured, nor they provide an uncertainty estimate. Second, the modelled reactivity (which model? a model is also mentioned on page 4 and Supplement B but no details are given anywhere) is more than a factor of 2 higher than the measured reactivity and the authors explain the discrepancy by saying that it is "likely" due to the uncertainty in the limonene standard. A factor of 2 would imply that there is a major issue with the limonene standard used. Therefore I am not sure what conclusions could or should be drawn from Figure 9 and the associated discussion.

Section 3.6 (ambient data). Two days of data from a branch enclosure experiment are shown in Figure 10, but the discussion is severely lacking. The authors mention, but do not show, concurrent observations of BVOC: even if they will be the subject of a future paper some data should be shown here, as they can help understand how well the instrument is performing. The authors also mention, but do not show or elaborate, that reactivity and "normalized reactivity" are different by a factor of 3. As I mentioned before, the need for normalization should be justified, it should also be explained why the normalized data are so different, and what does it mean for the interpretation of the results presented here.

## MINOR COMMENTS

Figure 8: please do not use "ppt" to indicate "parts-per-thousand". It is normally intended to mean "parts-per-trillion".

line 578: what "protective film"? Please be more specific.

line 603: "OH" not "ozone" scrubber.