

Atmos. Meas. Tech. Discuss., referee comment RC2  
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## Comment on amt-2021-354

Anonymous Referee #2

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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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Helmig et al. present the development of a total ozone reactivity monitor (TORM) for the direct determination of the ozone reactivity of vegetation emissions. The authors first describe the method and the modification brought to the system to minimize errors and interferences. A commercial UV absorption monitor has been modified to measure directly the difference of ozone before and after the reactor instead of using two monitors. In addition, Nafion dryer membrane tubing have been used before the two inlets of the monitor to reduce the known interference from water vapor of this kind of instrument. The authors then present the different tests they conducted to characterize the instrument including ozone loss on the vessel walls, pressure difference between the two channels of the instrument, evaluation of the modified monitor, estimation of the residence time, assessment and mitigation of humidity effects. The authors finally present some application examples including the measurement of ozone reactivity of test mixtures and samples from vegetation enclosures. On the whole, the characterization tests performed are not well described and appear insufficient to ensure the good quality and reliability of the measurement of ozone reactivity conducted by the instrument. Nevertheless, this manuscript is within the scope of AMT and will be of interest for the atmospheric community. I therefore recommend publication in AMT but after major revision.

### Main comments:

1) The authors described the setup of the two instruments with four flasks of 2.5L but no explanation is given on this choice. Why four flasks in series and not one or two bigger flasks of the same volume? This setup does not seem to be optimal and the part where a loss of reactants (ozone or biogenic VOCs) can occur is multiplied.

The wall loss is partially explored by the authors in the section 3.1 (system conditioning) where a procedure for passivation of the system with ozone is performed. However, the

authors stated that the loss wall was reduced to 1-2 ppb and did no longer show any drifts in the signal (P13, L630-631). It is not clear if this 1-2 ppb loss of ozone is something that remain constant over time after conditioning of the system and that is reproducible from one experiment to another and how is it taken into account in the measurement?

To complete this wall loss assesment, estimation of the wall loss for VOCs is also needed, especially for monoterpenes and sesquiterpenes, to determine how it impacts the ozone reactivity measurements?

2) In section 3.2: Balancing of the ozone monitor inlet pressures, the authors report an ozone differential signal of 1.7 ppb between the pre- and the post-reactor inlet. What is the cause of this difference? How is it taken into account in the measurements? Does it correspond to the 1.7 ppb subtracted from the measurement in the application examples (P 21, line 787-788). If it is the case please clarify. What is also not clear is how often this "background" is measured and does it remain constant over time? What is the procedure applied if differences are observed for this background before and after an enclosure experiment?

3) In section 3.5: Evaluation and Mitigation of humidity effects, the authors report a residual ozone reactivity signal response of 0.5 ppb for the differential monitor over a range of relative humidity of 10 to 84% and a residual response six times larger for the two-monitor instrument. This difference in interference is also observed in supplement G. Since both system were sampling through the Nafion tubing, what is the explanation for such difference in the interferences observed by both systems? How the remaining humidity interference observed for the differential monitor is taken into account in the measurement of ozone reactivity?

4) In section 3.6: application examples, the authors compare the ozone difference measured by the TORM and theoretical ozone depletion expected from the reaction of ozone with introduced limonene considering theoretical limonene concentrations, reaction rate constant and theoretical residence time. This comparison resulted in large discrepancy between the theoretical and the measured ozone depletion. The authors explain this discrepancy by the fact that the concentrations of limonene inside the cylinder is uncertain and is expected to have decreased with time. Furthermore, the authors used the theoretical residence time determined from the volume of the reactor and the flow rate.

First, why using the theoretical residence time since this latter was determined experimentally?

Then, this test is very important to perform a quality control and to ensure the reliability and good quality of the measurements performed by the TORM instrument which is not possible with the experiment shown in the paper. I would therefore suggest to perform again this experiment but with certified and known amounts of a BVOC or even better repeat it for several BVOCs (monoterpenes and sesquiterpenes) to check the response of the instrument and compare it to an accurate theoretical ozone depletion. I also suggest to use the residence time determined experimentally for the calculation of the theoretical ozone depletion.

**Minor comments:**

-P3, line 428: Change "methyl chavicol can be an important emission" for "methyl chavicol can be strongly emitted"

-P3, line 433: Change "BVOC emissions" for "BVOC concentrations"

-P10, line 578: "Flasks are covered with a protective film".

What is this protective film made of?

-P10, line 579-580: "one valve connects to a dip tube that leads to the inside on the opposite side of the flask (Fig. 4)". This is not visible in Fig. 4. Please remove the reference to the figure or use a picture in Fig. 4 where it is visible.

-P12, line 603: Change "ozone scrubber" for "OH scavenger".

-P16, Figure 6: The results in panel b are hardly visible. Please modify this panel to improve its quality. Please use reasonable significant figures for the linear fit equations in panel C.

-P17, lines 713-715: "Nonetheless, the residence time of  $\approx 120$ s for the normal plumbing configuration is sufficient to meet the requirements for the ozone reaction experiment"

What do you mean by sufficient? Please clarify and be more specific.

-P21, line 780: Change "reported" for "theoretical".

-P21, Figure 9: Please modify the format of the number of the x axis to scientific notation. Please use reasonable significant figures for the linear fit equations.

-P22, lines 807-808: Change "25 parts per thousand" for "2.5%".

-P25, Figure 11: This figure is of poor quality, please modify it to improve its quality.