

Ozone Reactivity Measurement of Biogenic Volatile Organic Compound Emissions

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Response to Anonymous Referee #2

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.

We are grateful for the comments from the referee. We have revised our manuscript to better describe the tests performed and demonstrate the performance of the ozone reactivity measurements. Following are the detailed answers to the comments (in italics).

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 original manuscript states that “The glass flask reactor design was chosen because it was deemed more compact and robust for field deployment applications.” (lines 572-574). In addition, they “have been developed and extensively tested for their inertness and purity towards atmospheric trace gases” (lines 576-577), which includes biogenic BVOCs. Because these flasks were available in the CU laboratory, they were selected for the reactor design. These glass flasks have proven to be the most inert material for collection of greenhouse gases. Air samples are collected in these flasks from sites all over the world and then shipped back to the Boulder NOAA lab for analyses, at times six months after sample collection. Pollmann et al. (2008) demonstrated storage of hydrocarbons in these flasks for a period of up to one year. These flasks are among the most inert air sample storage vessels known. BVOCs that reach the reactor through the sampling lines from the branch enclosure are unlikely to be lost to the inert walls of the flasks given they are placed in a heated housing and the relative short residence times. We added this information as motivation to the design of the reactor/choice for the flasks.

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?

In the revised manuscript, we now discuss in detail that this value remained constant for a given setup as long as the conditions in the system remain the same.

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

We did not perform BVOC recovery experiments in the flow reactor. Most of the surface area of the reactor is borosilicate glass, which is about the most inert wall material for VOCs that is known (please also see our response to the previous comment). Further, the reactor was slightly heated, which further reduces wall losses of heavier VOCs. For instance, we previously demonstrated storage of VOCs to up to 14 carbon atoms over 2+ years in a heated Aculife-treated aluminium cylinder (Helmig et al., 2004).

Residence times in the experiment here were much shorter, on the order of minutes, i.e. only approximately $1/10^7$ of the longest time that was tested in the referenced experiments. Furthermore, as already stated above, we consider it unlikely that BVOCs

that are volatile enough to be purged out of the branch enclosure and reach the reactor through the sampling lines are subsequently lost to the glass walls of the heated flasks.

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?

In the original manuscript, “Background” referred to the differential signal in the absence of reactive species (e.g., zero air measurements) and correspond to wall losses of O₃ in the reactor. This value can vary at the beginning of the experiment as the system equilibrates and when the flow through the reactor is modified. This is now explained in more detail in the revised manuscript. The ozone wall loss was determined regularly in the field by conducting measurements with scrubbed ambient air and an empty bag. Those measurements were then used as the reference/zero value for vegetation enclosure experiments.

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?

The schematic of the instrument was misleading. Nafion dryers were used only for the direct monitoring of the differential signal with one monitor. We did not dry the sample air when two monitors were used. The difference for the two-monitor signal stems from the differences in the response of the two monitors to the change in water vapor in the sample stream. Since two instruments will likely respond different towards humidity changes, there is a high likelihood that the effect on the difference in the signal between the monitors is going to be larger (unless the effects happen to cancel each other out). We have updated the schematic of the instrument in the revised manuscript.

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?

In the revised manuscript, however, we establish that the peak residence time corresponds to about 80% of the theoretical residence time for the instrument. The paragraph in section 3.6 and Fig. 9 have been updated accordingly.

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.

None of the manuscript authors are currently employed by the University of Colorado and the laboratory and instrument are no longer available for further experimental work. This research, however, is continued at Helsinki University. The proposed experiments are planned to be conducted by the Finnish group in their future TORM research and then be reported in a future publication.

Minor comments:

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

We changed the sentence according to the referee’s suggestion.

-P3, line 433: Change “BVOC emissions” for “BVOC concentrations”

We replaced “emissions” with “concentrations”.

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

What is this protective film made of?

The protective film is a shrink tubing material.

-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.

We rephrased the sentence.

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

We changed the sentence according to the referee’s suggestion.

-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.

We have updated the figure accordingly to the referee's recommendations.

-P17, lines 713-715: "Nonetheless, the residence time of ≈ 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.

In this context, it was meant that the residence time should be long enough to allow for O_3 to react with the BVOCs sampled and give a large enough differential signal that can be measured with enough precision with the given TORM configuration. We have rephrased this sentence differently in the revised manuscript.

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

This change was implemented as suggested change.

-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.

We have updated the figure according to the referee's recommendations.

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

We implemented the change.

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

We have improved the quality of several figures in the revised manuscript, including Fig. 11.

References cited

Helmig D., Revermann T., and Hall B. (2004) Characterization of a pressurized C5-C16 hydrocarbon gas calibration standard for air analysis. Anal. Chem. 76, 6528-6534.

Pollmann, J., Helmig D., Hueber J., Plass-Duelmer C., and Tans, P. (2008) Sampling, storage, and analysis of C2-C7 non-methane hydrocarbons from the US National Oceanic and Atmospheric Administration Cooperative Air Sampling Network glass flasks. J. Chrom. 11988, 75-87.