

Ozone Reactivity Measurement of Biogenic Volatile Organic Compound Emissions

Detlev Helmig^{1,2*}, Alex Guenther³, Jacques Hueber¹, Ryan Daly¹, Wei Wang¹, Jeong-Hoo Park¹,
Anssi Liikanen⁴, Arnaud P. Praplan⁴

¹Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA

²now at: Boulder Atmosphere Innovation Research LLC, Boulder, CO 80305, USA

³University of California Irvine, CA, USA

⁴Atmospheric Research Composition, Finnish Meteorological Institute, 00101 Helsinki, Finland

*corresponding author: dh.bouldair@gmail.com

Manuscript submitted to

Atmospheric Measurement Techniques

Response to Anonymous Referee #1

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.

We thank anonymous referee #1 for their assessment of our manuscript. Considering their comments, we have revised the manuscript to address their concerns, especially regarding the lack of information, the inconsistencies, and errors highlighted in this review. We added more description to the discussion of the residence time and the calculation of the ozone reactivity, and we provide more explanation of the model. Following are the detailed answers to the reviewer's comments.

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).

We added new text that explains in more detail the evolution of the experimental systems and the collaborative work between the U.S. and Finnish groups. We also clarified which experimental results are from which instrument. We consider the international U.S. – Finnish collaboration a strength of this work. This is now emphasized more in the revised manuscript text. Students and postdoctoral scientists from both countries participated in this research. The Finnish group visited the CU Boulder group for a full month to get trained in the instrument design and its operation. Several of the described experiments were conducted during this academic exchange. A joint field campaign was conducted two years later at the University of Alaska Toolik Field Station. Experimental results from the CU and Helsinki instruments were compared on several occasions. The parallel development and comparison of results from the two systems add confidence in the instrument performance and reproducibility of the measurement.

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.

The referee is right that a simple analytical solution is available. The use of the Taylor series is meant to provide a more elegant formula to calculate ozone reactivity. As $\Delta[O_3]$ is always much smaller than $[O_3]_0$, the condition for applying the Taylor function is always fulfilled (typically $\Delta[O_3]$ is only a few percent of $[O_3]_0$). In this case, the Taylor function leads to the same values as the exact analytical solution. We rephrased the mathematical treatment in the Supplement A to reflect this.

In addition, we reviewed our use of the term “ozone reactivity” for $\Delta[O_3]$. We now refer to it as “differential signal” instead where appropriate in the revised manuscript.

A few comments on the technical side of the instrument.

1) I don't quite understand what the advantage is 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.

We did not intend to claim that the design of the reactor lead to improvements over other similar instruments. The main claim of our manuscript is that the improvement comes from the use of an ozone monitor in differential mode. As highlighted by the reviewer, the main idea was to have a compact and portable system. These flasks were readily available in the CU laboratory and were selected for practical reasons and for their known “inertness and purity towards atmospheric trace gases”, as mentioned in the manuscript. The number of flasks (4) was chosen in order to reach a volume of 10L, so that the residence time in the reactor in this configuration is enough to ensure a large enough measurable differential signal. Furthermore, the use of four flasks is a compromise: fewer flasks lead to a “sharper” distribution for the residence time (see section 3.4) compared to using more flasks (“wider” distribution), but the volume would be too small to ensure a clear differential signal. Furthermore, the use of four flasks with dip tubes ensure “efficient purging and replacement of the air volume inside the flasks with minimal mixing” as mentioned in the manuscript. Four flasks also were a very good fit for using up the available space in the insulated Pelican box that was chosen for the reactor storage container.

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 "O₃ 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.

The volume of the mixer and the tubing leading to the reactor is estimated to be about 15 ml. At a flow rate of 5 L min⁻¹ (total prior to sampling before the reactor), the residence time in this small volume is very short (negligible), on the order of < 0.2 s, which is a small (i.e. negligible) fraction (~ 0.1 %) in relation to the overall residence time of ~ 150 s. We added a sentence to the manuscript to address this.

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.

Indeed, the instrument has been used in various configurations during testing, which also affected the flow through the reactor and the residence time, for instance when additional monitors (for O₃, and the fast NO monitor) were added after the reactor. A target flow of 4 L min⁻¹ was chosen to yield a large enough residence time through the 10 L reactor and a well measureable differential ozone signal. The annotations in Figs. 3 and

5 were not accurate and have been updated in the revised manuscript. Figs. 3 and 5 now show the instrument operated in the default configuration with flow through the reactor of 4 l min⁻¹. Other occurrences have been corrected in the manuscript. For most experiments and tests, the flow was around 4 l min⁻¹ and is reported accordingly, as for instance, on page 22.

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.

There seems to be an important misunderstanding. "limit of detection" and "sensitivity" are meant to be two different things and we do not use them interchangeably. Limit of detection is the smallest ozone differential signal that can be quantified with confidence outside of the noise range of the differential ozone signal determination. The LOD was determined as three standard deviation of the delta ozone signal variability during sampling of clean, BVOC-free air. The hourly standard deviation values for delta ozone were 0.075 - 0.096 ppb and are discussed in section 3.1., yielding a delta ozone LOD of 0.23 – 0.29 ppb.

Sensitivity (note that from here on, we substitute this term with 'response') defines the ozone differential signal per reactivity of BVOC in the sample flow. An upper threshold of the sensitivity was calculated from the experiment with the limonene standard. The slope of the Figure 9 graph depicts the delta ozone as a function of the ozone reactivity (R_{O_3}), as determined from the theoretical limonene mole fraction multiplied by its ozone rate constant. The linear regression slope value using the experimental values accounted to 6.2×10^3 ppb s assuming a 20 ppm mole fraction of the standard. This should be considered a lowest case estimate. If, for instance, the actual mole fraction of the standard was half of its preparation value (10 ppm), the slope value of the regression would account to 1.2×10^4 ppb s. Figure 9 also depicts the theoretically expected behaviour of delta ozone versus the ozone reactivity (at 20 ppm standard mole fraction) based on the assumption of perfect mixing and the experimental residence time. There is approximately a factor of 2 difference between the two data series. The theoretical regression result (1.4×10^4 ppb s) would be the response value if this difference is due exclusively to the standard having a lower mole fraction than the one assumed from its preparation.

We have added more explanation of these two terms in the text. Further, in order to avoid this confusion, we replaced the term "sensitivity" with "response" where applicable.

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.

In the revised manuscript, we have clarified that the 1.7 ppb value is valid for the specific configuration for which the pressure balancing was performed. Discussing Fig. 6B, we now mention that this value can vary according to the instrument conditioning and configuration.

For simplicity, Fig. 5A does not include the setup for the counterflows of the Nafion driers. Figure 5B on the other hand depicts only the plumbing for these counterflows. Therefore, the valve in Fig. 5A (Teflon) is the one used for pressure balancing and the valves in Fig. 5B (stainless steel) are the ones used to make sure that the counterflows in the Nafion driers are 2 to 3 times the sample flow. As mentioned, the valve in Fig. 5A is made of Teflon, so that this added control of the pressure does not cause a significant loss of ozone. As no sample flow goes through the stainless-steel valves in Fig. 5B, they do not affect ozone measurements in any way. The caption of Fig. 5 has been updated to clarify this.

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(O₃) from an empty chamber (figure 6B) is often higher than the measured Delta(O₃) (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?

Normalizing the reactivity measurements to the air flow and the weight of the leaves' biomass allows for the determination of the ozone reactivity of biogenic emission rates and their normalization to the leaf biomass in the experiment. This is meant to allow for comparison with other subsequent studies.

We revised thoroughly Fig. 6 to make it easier to read. "API" referred to the ozone monitor model of that was used after the reactor in this specific configuration. This was done in order to compare the two approaches to measure $\Delta[O_3]$: (1) with two monitors and (2) with a differential analyzer. We now refer only to "two monitors" and "differential" $\Delta[O_3]$ for better clarity.

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.

Changing the flow through the reactor in the reverse direction was done to assess (see line 706) the effect of the dip tube on the flow characteristics of the system. The test confirmed that introducing air through the dip tube results in a narrower distribution for the residence time (lines 716-717), which is advantageous for the purpose of the experiment.

A set of tests were performed to characterize and improve the experiment. Those at times required a different plumbing as the default configuration, which affected the flow through the reactor. However, the experimental determination of the residence time as described in section 3.4 was performed only with one system configuration with flows of 4 and 6 l min⁻¹ through the reactor, with 4 l min⁻¹ used in the default configuration as clarified above. There are various ways to define the residence time, as also discussed by Sommariva et al. (2020), and as depicted in Fig. R1 below. It can be (1) the time when the signal starts to increase, (2) the mode of the distribution, i.e. the most frequent residence time, (3) the mean of the distribution, and (4) the theoretical residence time based on reactor volume and flow rate calculation. In the original manuscript, we used the definitions (2) and (4), leading to the inconsistencies pointed out by the referee. In the revised manuscript, we explain that we use the mean of the residence time distribution (3) for ozone reactivity calculations. These times are 132 s and 79 s for the 4 and 6 l min⁻¹ flows, respectively. This corresponds to fractions of 0.88 and 0.91 of the theoretical residence time. When the flow through the reactor deviates from 4 or 6 l min⁻¹ at which we have experimental data, we applied a factor 0.9 to the theoretical value in order to utilize a residence time that is more in line with the experimentally determined value.

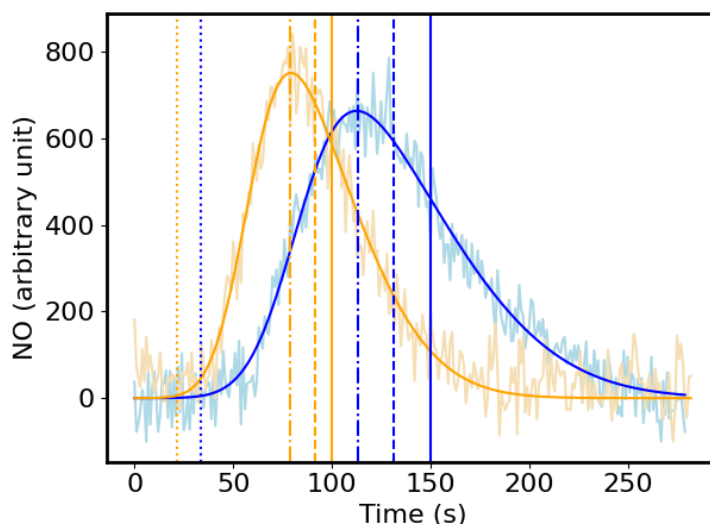


Figure R1. Response of the fast NO monitor placed after the reactor after injection of NO in the reactor flow for 4 and 6 $l\ min^{-1}$ (in blue and orange, respectively).

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).

The first reviewer comment relates to the introduction section. We added references to Wilson and Birks (2006) and Spicer et al. (2010) studies there as well.

The statement in lines 691-692 was meant to explain that if the determination of the ozone loss in the absence of chemical gas phase reactions (previously referred to as "background", but now for better clarity termed "ozone wall losses" are performed at a similar RH as the ozone reactivity measurements, the Nafion dryers ensure a negligible interference despite changes in RH. This is now clarified in the manuscript. One should also emphasize that during real applications the dynamic range of humidity changes is generally smaller than the wide range that was tested in the lab experiment. Scrubbed ambient air, with ambient RH levels, was always used for zero tests.

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.

It is true that the large uncertainty in the mole fraction of limonene is unfortunate. However, this experiment still serves the purpose for demonstrating the linearity of the system's response to a linear increase in the limonene, despite not knowing the absolute mole fraction. The model mentioned here, on page 4, and in supplement B is a simple box model using reactions of BVOCs with O₃ and solved with a Kinetics Pre-Processor. It is meant to estimate the O₃ decay in the reactor (i.e., Δ[O₃]). We added a paragraph to clarify this in the methods section.

As the limonene standard was prepared in house and had been stored for a relatively long time and it was prepared in a non-specialty treated cylinder, it is not unrealistic to assume that the mole fraction could have decreased by a factor two.

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.

Indeed, the idea of this section was to showcase the data from the application of a branch enclosure experiment. Allocating the observed ozone reactivity to individually identified BVOCs will be presented in a follow-up manuscript that is currently in preparation.

The sentence regarding the normalized reactivity was unclear and has been edited in the revised manuscript. We meant to state that there is a variation up to a factor of three for the normalized reactivity for the various tree species investigated.

MINOR COMMENTS

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

This was a spelling error. We intended to use "ppt". We now use the permille symbol (‰) in the revised manuscript.

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

The protective film is a polyolefin shrink wrap (buyheatshrink.com).

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

We replaced “ozone scrubber” with “OH scavenger”.