

Manuscript title:**Ozone reactivity Measurement of Biogenic Volatile Organic Compounds Emissions**

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Answers to the referee comment

We are grateful for the referees' and editor comments and have addressed them as best as we could in the latest version of the manuscript. Below are our more detailed answers to the referees' concerns. The referees' comments are in italics font and our answers in regular font.

Referee #1

The authors have addressed almost all of my concerns from the previous version, as well as those of the other reviewer. However, I am still concerned by the comparison between the ozone difference observed by the TORM and theoretical ozone depletion expected from the reaction of ozone with introduced limonene presented in section 3.6. Since this comparison leads to large discrepancy between measured and theoretical ozone depletion probably due to unknown Limonene concentration introduced in the system and since the authors are not in capability of performing again this experiment with a certified standard the outcome of this experiment is very low. If the purpose was to demonstrate the linearity of the TORM response, I would recommend to keep the measurement only and to remove the theoretical value since the comparison brings more confusion than interesting results and to rewrite this section accordingly. The author could also add a sentence to justify the absence of calculation of theoretical value due to uncertain amount of Limonene introduced in the instrument.

As both referees agreed that Fig. 9 is not compelling due to the uncertainty of the limonene concentration, we removed references to the mixing ratio of the test gas from the text as well as the comparison with the modelled values and are now only focusing on the linearity of the system response and use the MFC flow of the standard for the x-axis scale.

Referee #2

The manuscript has significantly improved compared to the initial version, but there are still a couple of problematic points.

The main concern I have is about Figure 9 and the associated discussion. I understand that one of the points is to show the linearity of the response. But this is not (or rather not only) what the figure is showing. The x-axis indicates a "theoretical ozone reactivity" in s⁻¹, which strongly implies that is the expected reactivity based on the amount of BVOC sampled. This is highly misleading given that the authors admit that they don't know the exact amount of BVOC used in the experiment (line 482). My suggestion is either to remove Figure 9 entirely (and the corresponding lines 476-499) or rework the figure to use arbitrary units on the x-axis and reword the text (including in the conclusions and abstract)

to make clear that this is just to show linearity of response and to remove all references to actual reactivity values.

As referee #1 expressed the same concern, we have followed the advice from both referees and simplified Fig. 9 as well as the discussion associated with it by removing any reference to specific mixing ratios of the limonene test gas and instead focus on showing the linearity of the response.

The second issue is with the way the authors seem to use the difference between ozone measurements before /after the reactor (delta) and ozone reactivity. Although the instrument presented here measures O3 reactivity, most of the discussion and the figures are about delta ozone. The two parameters are related, but they are not equivalent and should not be treated as such. Additionally, I think that the way the authors calculate reactivity with the equations in Supplement A is unnecessarily complicated, but I concede this may be a personal preference. In any case, I suggest that the authors calculate the reactivity from delta ozone, and amend the figures, captions and text accordingly because reactivity is the variable that is the focus of the paper and the objective of the instrument.

We unfortunately do not fully understand the referee's comment. What the instrument measures, physically, is $\Delta[\text{O}_3]$, and the total ozone reactivity is derived from this value. For this reason, we discuss in sections 3.2 to 3.5 the effect of pressure, differential measurement, residence time and humidity on $\Delta[\text{O}_3]$, including ways to eliminate or mitigate errors during the measurement of this physical parameter. Figure 6 shows $\Delta[\text{O}_3]$ as its objective is to show the difference between a two-monitor system and the use of the differential monitor.

The way we calculate total O_3 reactivity (RO_3) is the same as in Matsumoto (2014), eq. (6) and Sommariva et al. (2020), eq. (4). These are the same calculations as our eq. (S5). The derivations of these equations vary slightly between the publications, but ultimately describe the same calculation. We simply made the derivation explicit in Supplement A. We understand that the reviewer thinks that the approximation that we use to derive eq. (S6) is unnecessary, but we believe that it is an elegant way to calculate RO_3 . It also highlights that under the operating conditions of TORM ($\frac{\Delta[\text{O}_3]}{[\text{O}_3]_0} < 0.1$), RO_3 is linear to $\Delta[\text{O}_3]$. RO_3 is derived from equation (S6) for the measured $\Delta[\text{O}_3]$, the fixed amount of ozone getting into the reactor ($[\text{O}_3]_0$), and the given residence time (Δt), taking into account wall losses. Because of this linear relationship, any plot with either $\Delta[\text{O}_3]$ or RO_3 would look the same, besides for the axis scale.

We updated Fig. 10 in section 3.6 on TORM's applications to include RO_3 as well. We want the reader to understand, though, that in some cases, especially with emission measurements that can include fast reacting compounds (i.e. with ozone reaction rates similar to the one of NO), the total O_3 reactivity derived from TORM measurements with equation (S6) would yield a lower reactivity value than expected from the mixing ratio of the fast reacting compound and its reaction rate with O_3 (k_{O_3}). This is what we wanted Supplement B to illustrate. We are planning to discuss this aspect in the subsequent publication where measured RO_3 with TORM and calculated RO_3 (from BVOC measurements) will be compared, but we thought that it would be important to be mentioned here as well.

It is true that while Fig. 11 y-axes were labelled "R(O3)", the actual data in the figure were normalized $\Delta[\text{O}_3]$. We have updated the figure so that it now shows the normalized measured total O_3 reactivity, and the discussion has been slightly altered to reflect this change.

MINOR POINTS

Figure 2: correct "Pluming".

We have fixed the spelling error in Fig. 2 in the revised manuscript.

Line 263: please add a number. How much is "negligible"?

We estimated that the residence time in the tubing is in the order of milliseconds, which is several orders of magnitude smaller than the residence time in the reactor. We have included this information in the text of the revised manuscript.

Lines 276-279: there is not enough information about the model. Is it assuming only the first step of ozonolysis or does it include the complete oxidation mechanisms? In this case which chemical mechanism was used?

As Fig. 9 does not use the modelled data anymore, the description of the model was moved from the methods section to Supplement B. There we have added that no secondary chemistry is considered because the typical residence time in the reaction is of a few minutes so that we use the reaction rates at room temperature listed in the legend of Fig. S1. This is now explicitly stated when describing the model.

Figure 10: is this the same experiment shown in Figure 6? please clarify in captions and text, as appropriate.

We regret that this was not clear enough. As stated in the text, Fig. 10 data are from field experiments at the University of Michigan Biological Station (UMBS). This information is now also included in the caption of Fig. 10 in the revised manuscript.

Figure 11: The caption says "delta ozone" and the label on y-axis says "R(O3)". Please correct.

The reviewer correctly noticed a discrepancy (as discussed above). Despite the y-axis stating "R(O3)", the plotted parameter was a normalized $\Delta[\text{O}_3]$. The figure has been updated so that it now shows the measured total O_3 reactivity of the emissions (i.e. normalized to the leaf dry weight and the flow through the branch enclosure). These are the measurements from the same field campaign as Fig. 10. This has now been clarified with the addition of the location of the measurements in the figure caption.

Supplement C: it would be good to show some results of the testing of the differential monitor setup. Was the metering valve used in these tests? If not, why was it not necessary, but it is required in the standard setup?

The setup presented here is only meant to present how the differential monitor was compared to two independent monitors. This configuration was used in most of the tests performed in this manuscript, except for the ones done with the instrument from the Finnish Meteorological Institute, which use the one-monitor (differential) TORM configuration for the delta ozone determination (but with a second monitor sampling the inflow into the reactor to monitor the absolute value of ozone getting into the reactor, not shown in Fig. 3).

A metering valves was used for all the tests, and it is simply a simplification that it was not displayed in this schematic. Fig. S2 in Supplement C was corrected in the revised manuscript.