

Response to Anonymous Referee #2

A. General comments:

In this manuscript, authors focused on total ozone reactivity, built and characterized their instrument in the laboratory, and tested it in the glasshouse. This study is positioned as a basic research of the instrument and a demonstration for measuring BVOCs emission from plants. Ozone reactivity of BVOCs is interesting for investigating BVOCs. Thus, the reviewer believes that this work has an important implication and is significant enough to be published in this journal. However, the present manuscript leaves several points to be improved, clarified, modified, and/or reconstructed, in order for readers to understand descriptions and to recognize the significance of this study clearly. Especially, it is necessary to correct critical errors on quantitative descriptions, to indicate more information and explanations, and to clarify the story of discussion which authors want to express during the demonstration of the instrumental test.

We thank the referee for the detailed comments and suggestions. Below are our responses and related modifications to the manuscript. The line numbers refer to the version of the manuscript published on AMTD.

B. Important specific comments:

B1) Line 101 and followings: Quantitative descriptions on contribution of NO₂ should be corrected. The reviewer thinks that 1 ppbv of NO₂ corresponds to $3.52/9.6 = 1/2.7 = 0.37$ ppbv of a-pinene and $3.52/22 = 1/6.25 = 0.16$ ppbv of limonene, respectively. And then, consequently, based on the correct values, descriptions on importance of nighttime NO₂ should be checked again, including descriptions in Sect. 5. Please do not mislead readers.

We thank the reviewer for spotting this error which has been corrected. The point, however, stands: the formation of NO₃ (and hence the loss of O₃ to NO₂) is significant only when NO₂ concentration is high, which is largely not the case in the conditions TORS was designed for.

Lines 102-103 were modified to: "This means that NO₂ can be a significant ozone loss during the night only when its concentration is high, which is not usually the case in unpolluted forested environments."

For the impact of NO₂ on the glasshouse measurements presented in Section 5, see below.

B2) Fig.1 and Lines 160 ~ (descriptions on model estimations) : Please show more information and descriptions on model estimations. For example, how much is the initial OH concentration? Why does the delta-OH in Fig.1 distribute less than zero? At all, what is 'delta-OH' in Fig.1? (No descriptions and explanations in sentences.) Additionally, please add descriptions on the applied reaction time in the sentence and in the caption of Fig.1.

We recognize that Figure 1c (and related text) could be clearer, so we have changed it to show instead the mean OH concentration at each concentration of a-pinene as a function of initial cyclohexane. The corresponding paragraph in Section 2.3 (lines 170-177) was modified as follows:

"The average modelled concentrations of the OH radical at different levels of cyclohexane are shown in Fig. 1c. In the absence of cyclohexane, the model calculated OH concentrations between 1.3×10^6 and 4×10^6 molecule cm⁻³ for a-pinene mixing ratios of 0.1 ppb and 50 ppb, respectively. With addition of the OH scrubber, the simulated concentration of OH in the reactor decreased by 2 orders of magnitude at mixing ratios of cyclohexane between 1 ppm

(for α -pinene <5 ppb) and 10 ppm (for α -pinene = 50 ppb). Increasing the cyclohexane mixing ratio above 10 ppm did not cause further decrease in the calculated concentration of OH, nor a reduction in the loss of ozone and α -pinene (Fig. 1a-c), at least within the range of α -pinene concentrations explored by the model.”

B3) Line 204: Why and how can 'ambient temperature and pressure' affect the chemistry inside the reactor? Now there are no explanations in the manuscript.

Temperature and pressure affect the rate coefficients of the reactions that take place inside the reactor. The sentence has been corrected to: “and, to a lesser extent, ambient temperature and pressure (which influence the rate coefficients of chemical reactions). To date, the effect of temperature and pressure is negligible, as the system has been operated under near-ambient conditions.”

B4) Line 258 'simultaneously' : How did authors check and ensure the simultaneity? Uncertainties on the timing of the synchronized injection of acetone can cause uncertainties on the determined reaction time.

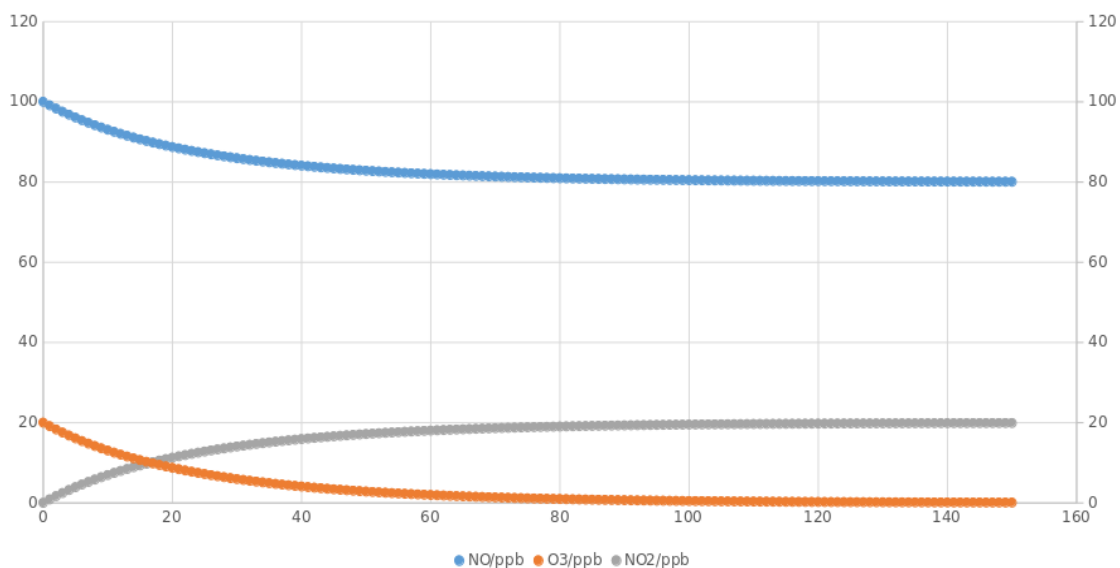
The injections were made manually by two different persons using a timer for synchronization. The reviewer is correct that this procedure has inherent uncertainties, however the time difference is such that these are very small. For a residence time of 164 seconds (Figure 3) a discrepancy of, for example, 0.5 seconds in the injection times results in an error of ~0.3%. The other approaches also have their own uncertainties and assumptions, which is the reason we have used three different methods to determine the residence time.

B5) Fig.4 & Sect.4.1 (especially, on NO+O₃ reaction): In 'Method 2 (Fig.4a)', $k[\text{NO}]$ up to 0.05 (maybe in the unit 's⁻¹'? please clarify the unit;) were adopted. It means that [NO] up to about 100 or 110 ppbv, I think. I want to know authors' opinions on following questions and for authors to revise the descriptions to clarify the situations:

[Q1] Concentrations of NO and O₃ are similar. The reaction NO+O₃ is fast. Then, both NO and O₃ can significantly decrease within the reaction time. (Question:) Are the settings of the experiments, calculations, and discussion to determine the reaction time proper to realize and ensure the 'pseudo first-order reaction' as described in Line 267 ? When I tried a rough and simple calculation on the decrease of O₃ and NO, for example, till $t = 150$ sec, NO decreased from 100 ppbv to 5 ppbv and O₃ decreased from 120 ppbv to 25 ppbv. NO can drastically decrease during the reaction time due to its fast reaction with O₃.

The experiments with NO were conducted at lower concentrations of O₃ (~20 ppb) than the normal operating conditions of TORS. During the reaction time the concentration of NO therefore dropped only to 80-90 ppb. We do not think that the fact that these experiments were conducted at lower ozone levels than the other experiments is important, since they were only used to determine the residence time. The NO and O₃ concentrations used for these residence time experiments have been added to the text.

In any case, the reviewer is correct that the system deviates from pseudo first-order conditions during these experiments. We have reanalyzed the data with the help of a simple steady-state model. As shown in the Figure below, because the reaction between NO and O₃ is very fast, the concentration of NO decreases to 80 ppb within 60 seconds and, therefore, the initial concentration of NO is not representative of the NO concentration inside the reactor for most of the residence time.



We have therefore recalculated the residence time with method 2 using the average NO concentration over a period of 150 seconds, instead of the initial NO concentration. The results of this reanalysis are now shown in Figure 4 (the calculation using the initial NO concentration is also shown for just one flow, for reference). The residence time obtained in this way is closer to the residence time calculated assuming a plug flow (method 1) than the one obtained using the initial NO concentration. To make the analysis more robust, a best fit polynomial function (2nd degree) was calculated using all 3 methods and the results of the fit (140 seconds) has been used as the residence time for all the experiments in the paper. The new residence time is 9% higher than the one used in the original version of the paper, which is well within the estimated total uncertainty of TORS (32%). All ozone reactivities and ozone wall losses mentioned in the paper have therefore been recalculated (they are 9% lower) and the relevant figures corrected accordingly. Additionally, the following modifications were made to the text:

Line 267: added “Since the chemical system deviates from pseudo first-order conditions, the mean concentration of NO inside the reactor was used to analyze the experimental results.”

Lines 274-275: changed to “In the experiments described in Sect. 5, we used a value of 140 seconds for the residence time, determined by fitting a 2nd degree polynomial to all three methods, as shown in Fig. 4b for a reactor flow of 2470 sccm.”

The caption of Figure 4 was changed to “(a) NO reactivity experiments analyzed using the mean NO concentration inside the reactor. One experiment analyzed using the initial NO concentration is also shown, for reference. (b) Residence times as a function of reactor flow – determined by three different methods – and polynomial fit to the three methods (black dashed line). The results of the acetone injection method are taken from Fig. 3. The red star indicates the residence time used in this work (140 seconds for a reactor flow of 2470 sccm).”

[Q2] In Fig.4a, we can estimate the reaction time. For example, in case of 2470 sccm, for $k[\text{NO}] = 0.04 \text{ (s}^{-1}\text{)}$, $-\text{LN}(\text{O}_3(t)/\text{O}_3(0))$ is about 4, and the slope of the regression line is roughly found as $4/0.04 \sim 100 \text{ sec}$. However, for 2470 sccm in Fig.4b, we can read out the reaction time determined by NO reactivity as about 130 sec. Which figures are correct? And is the reaction time that authors determined and described in the manuscript exactly correct? These are critical points because the reaction time is one of the most important factors to determine ozone reactivity. Would you please confirm them and, as necessary, revise descriptions in order to clarify authors' standpoints?

Figure 4 has been substituted with a new version following the comments by the referee on the NO+O₃ experiments to determine the residence time (see above). Note that as a consequence of the modifications listed above, the residence time was changed throughout the paper to 140 sec (9% higher than the original value of 128 sec).

Additionally, as an associated question, what value of k(NO+O₃) was applied in this study? Authors indicate the values as '1.89x10⁻¹⁴' in Table 1 and '1.73x10⁻¹⁴' in Line 266. The ratio 1.89/1.73 is 1.09. If authors mistake the values of k, it results in ~ 10 % errors by itself.

The value used in this work is 1.89e-14, as recommended in the updated datasheet from Atkinson et al. (2004). The text on line 266 has been corrected.

B6) Fig.6a and Sect. 5.1.: Between calculations and experiments, the dependence on a-pinene concentrations can be seen different. Experimental data rise up steeply (a-pinene < 10 ppb) and then gradually increase (with smaller slope than calculations). Calculations show a straight line. Would you please explain briefly these results in the sentences? What happens in the reactor, do you think?

The ozone reactivity at a-pinene levels below 10 ppb is less than 2.3e-5 s⁻¹, which is lower than the interquartile range of the wall loss (see line 300), and corresponds to a drop in the O₃ mixing ratio inside the reactor of <0.4 ppb, which is less than the detection limit of the ozone monitors. Therefore we think that those data points are effectively indistinguishable from the instrument's noise.

The sentence at line 350 has been modified as follows: "At mixing ratios below 10 ppb of a-pinene, the measured reactivities cannot be statistically distinguished from each other and from zero; in fact, the corresponding reactivity (2.36e-5 s⁻¹) is of the same magnitude as the average standard deviation of R(wall) (Sect. 4.2)".

B7) Sect. 5.3, about NO contribution to ozone reactivity: It is unreasonable to understand that the present descriptions that NO concentration in the house is assumed as 20 % of ambient concentration (7 km far from the experimental site). We think that the assumption on NO concentration is conveniently and arbitrarily made. If authors have any information to validate it, it is necessary to show the evidence and to explain them clearly. If not, it is necessary to indicate clearly authors' opinion, procedures of analysis, flow of argument, and the positioning of this experiment. Especially, please distinguish between the fact and the interpretation. For example, the reviewer's understanding of this section is as follows . . . (Fact) This experiment is aimed at a challenging demonstration of the TORS instrument. The major point is ozone reactivity measurement. It is true that significant RO₃ was captured during the experiment. (Assumption & Caution) Authors want to discuss on BVOCs contribution to captured RO₃ data. To do it, NO contribution should be considered. However, NO concentration in the sample is not monitored. Then the monitoring data (7km far) were adopted in order to know rough information on NO concentration. However, NO concentration can vary largely in the urban area due to the location, traffics, time of day, etc. Thus, adopted NO concentration is arbitrary and has large uncertainties. (It is unfair if descriptions on the limitations are insufficient.) (Interpretation & Authors' opinion) (For example) To discuss NO contribution, NO concentration was assumed as 0 to 100 % of ambient (7km far) concentration. When NO was set to ?? % or more, ozone reactivity by NO is larger than captured RO₃. So it was suggested that NO concentration was less than ?? % of ambient level. In this study, as an upper limit (?), NO was assumed as 20 % of ambient level where NO contribution is equal to and/or less than captured RO₃ (Fig.9). Then BVOCs contribution to RO₃ was indicated as ?? in Fig.9.

B7-2) Line 441 'urban background site' and Line 457 '50m from nearby roads': Please clarify the positioning of each site. Is the background site far from roads (i.e. not 'roadside')? Is the experimental site also considered as 'urban background'?

B7-3) Fig.8: NO concentration data at the urban background site (or NO contribution to RO3) should be indicated, because they are essential for us to discuss NO contribution to RO3 in Fig.9. For example, does NO really show the daytime peak as Fig.9? Does NO indicate its variation similar to RO3? B10) Around Line 455, about the lifetime of NO by O3 reaction: k is about 2×10^{-14} , $[O_3]$ (30 ppb) is about 7.5×10^{11} , then $k[O_3]$ is about $1.5 \times 10^{-2} \text{ s}^{-1}$. Thus, the lifetime of NO is about 67 sec ($= 1/(1.5 \times 10^{-2} \text{ s}^{-1})$). This error is critical for the authors' consideration that NO can be reduced to 20 % of ambient level due to O3 reaction in the sample tube (4 sec). Associated to the comment B8, can ambient NO react with residual O3 in the glasshouse before the sampling inlet? Please consider them again and reconstruct the descriptions.

B7-4) Such authors' standpoint and assumptions should be noted at the beginning of the paragraph, as well as at the end. 'This is only a (challenging?) rough estimation & interpretation based on some assumptions', 'NO concentration is not monitored; NO contribution is assumed', for example. Also in the caption of Fig.9, such descriptions on 'assumption' are desirable.

B8) Sect. 5.3, about O3 and NO2 in the glasshouse: Authors consider that NO concentration in the house is smaller than ambient. Then, how about O3 and NO2 concentrations in the house? Is the glasshouse enclosed by walls? Or, can ambient air pass through the house? As a result, how much are O3 and NO2 concentrations in the house, do you think? Are O3 and NO2 in the house significant for RO3 measurement?

The reviewer is correct that the assumptions on NOx levels inside and outside the glasshouse, and the usage of monitoring data collected far from the observations (although under similar conditions), are speculative. Reviewer #1 also made similar comments.

In the absence of NOx measurements inside the glasshouse, this part of the paper was meant to be only qualitative, but we realize that we don't have enough information to support the assumptions made. The important point here is that the ozone reactivity measurements showed in Figure 8 do include a contribution from ambient NO, although we cannot quantify it. This implies that accurate NO measurements must always be taken alongside ambient ozone reactivity measurements.

Therefore, we have removed Figure 9 and lines 452-463 from the final version of the manuscript and changed lines 438-442 to: "Measurements of NO were not available inside the glasshouse, so it is not possible to quantify the contribution of R(NO) to the total ozone reactivity measurements shown in Fig. 8."

The caption of Figure 8 was changed to specify that the figure shows the sum of R(O3) and R(NO).

We have also added the following sentence to the conclusions (Section 6): "Moreover, our experimental data indicate that accurate measurements of NOx are always required to be able to interpret the TORS observations."

B9) Fig.9, about the diurnal variation of BVOCs contribution to RO3: Why does the BVOCs contribution indicate their peak during night (or before dawn)? Because BVOCs emission from plants usually depend on temperature and light intensity, it is expected that BVOCs

contribution to RO₃ has daytime peak. Would you please add explanations and your opinions on such diurnal variation of BVOCs contribution?

This is mentioned on lines 441-451. BVOCs emissions are higher during the day but OH concentrations are also higher during the day. Most BVOCs react more readily with OH than with O₃ and, as a consequence, the contribution of BVOCs to total RO₃ is reduced during the day.

C. Other comments and Technical corrections:

C1) Line 29: 'state' → 'states' ?

Corrected.

C2) Lines 64 - 65 and References: If authors want to refer the proceeding of a conference (Park et al.(2013), another earlier proceeding in the previous conference should be referred: Matsumoto, J.: Comprehensive analyzer for biogenic volatile organic compounds detected as total ozone reactivity, in AGU 2011 Fall Meeting, 2011.

The reference has been added.

C3) Line 71 'known BVOC mixture' → The reviewer cannot find descriptions on such 'mixture' in the following sections. Please clarify what the mixture is. (e.g. mixture of a-pinene and cyclohexane? but the scavenger is not BVOC . . .)

The sentence has been modified to: "laboratory measurements with known concentrations of selected BVOCs,"

C4) Line 90 (eq.2) and Line 105 (eq.3): Ozone concentrations, [O₃], are missing in all loss terms of ozone.

Corrected.

C5) Line 91 'R11' → 'R2', too? C6) Line 131 'R5-R8' → 'R6-R8'?

The hyphen indicates a range, so "R1-R11" includes R2, and "R5-R8" includes R6.

C7) Line 140 'Sect.4.2 → Sect.5.1, too?

The reference is to the experiments done to characterize the ozone wall loss, which are described in Section 4.2. Section 5.1 does not discuss the ozone wall loss, only the experiments with BVOCs.

C8) Line 146: Please add brief descriptions on 'Sommariva et al., submitted'.

The full reference has been added.

C9) Lines 178-184 and Fig.1d: In Fig.1d, RO₃(with)/RO₃(w/o) (please add the axis name in the figure) are ~ 0.965 at a-pinene = 0.1 ppb and ~0.950 at 0.5 ppb. That is, RO₃(w)/RO₃(wo) ratio decreases while a-pinene < 0.5 ppb, and then increase for a-pinene > 0.5 ppb. Would you please add brief explanations on this trend?

It is difficult to see because of the scale of the figure, but the point at 0.95 corresponds to 1 ppb of a-pinene not 0.5 ppb (the point at 0.5 ppb was actually missing from the figure because of a plotting error, which has now been fixed).

The values in the Figure are as follow:

Initial a-pinene mixing ratio (ppb)	ratio of R(O3) at 1ppm of cyclohexane to R(O3) without cyclohexane
0.1	0.96
0.5	0.94
1	0.95
5	0.98
10	0.99
50	1.01

In other words, for levels of a-pinene below 1 ppb, the effect of the OH scrubber is inversely correlated to the concentration of a-pinene, while above 1 ppb it is directly correlated (as the reviewer correctly points out). This is most likely due to the balance between OH production by a-pinene ozonolysis vs OH consumption by a-pinene and/or cyclohexane, which is different at different levels of a-pinene.

C10) Line 193 'ambient measurements' → Strictly, 'ambient, not always, but nighttime & high NO_x & low NO' ? Please clarify the conditions.

The reviewer is correct that high NO_x conditions are required, although we note that nocturnal conditions are not required, since the sentence refers to the reactions taking place inside the reactor, which is dark.

The sentence has been modified to: "NO₃ formation in the reactor is only an issue for ambient measurements under moderate or high NO_x conditions, not for laboratory, enclosure and environmental chamber experiments under low or zero NO_x conditions."

C11) Line 264 'about 30 %': It is true that '164 s' is 70 % of '228 s' and thus 30 % smaller than '228 s'. However, '228 s' is 139 % of '164 s' and thus about 40 % larger than '164 s'. The descriptions are not clear, including the word 'difference'.

The sentence has been changed to: "the residence times estimated using the "means" calculations are about 40% larger than those estimated using the "maxima" calculations"

C12) Line 267 'Eq.3' is not correct.

Corrected to "Eq. 5".

C13) Around Line 294: Please clarify, anywhere in the sentences earlier, what the 'central? 0.5 slpm flow of zero air (without O₃ lamp and scrubber)' in Fig.2 means. Then the mean of 'dilution' (Line 293) can be clear. (The zero flow may be used as 'dilution flow to control the concentration of ozone' as described in Line 312. However, before Line 294, we have not already recognized that point.)

We have amended Figure 2 to clarify the components of the system. Line 216 has been changed to: "An ozone flow is generated by irradiating a flow of zero air with a UV mercury lamp (UVP Ltd., UK); a zero air flow is added downstream the mercury lamp to control the concentration of ozone (Fig. 2)."

C14) Fig.8 'estimated HIGH & LOW': Why do these data indicate diurnal variation? How to determine these data?

The oscillations in the estimated reactivities are due to ambient temperature, which affects the calculation of the rate coefficients. The description of how these estimates were derived is on page 15 (Section 5.3).

C15) Scientific names of plants: Italics?

The scientific names of all plants have been written in italic.

C16) Line 470: It is desirable when conditions like averaging time and reaction time are also indicated.

Added on line 469: "with a residence time of 140 seconds, an averaging time of 5 minutes, and an estimated total uncertainty of ~32%"

C17) Table 1: If possible, please indicate the lifetimes of VOCs for $O_3 = 120$ ppbv. Then we can compare the lifetimes to reaction time and discuss the pseudo first-order reaction.

The table has been modified as suggested.

C18) Figures: Please add the names (titles) of axis.

Done.