

Response to Anonymous Referee #1

The authors present a description of an instrument to measure total ozone reactivity, details of experiments to characterise the instrument and initial results from measurements of the total ozone reactivity made using individual compounds, emissions from a single plant species, and in a glasshouse from several plant species. The manuscript demonstrates the potential for measurements of total ozone reactivity, but is lacking detail in some areas which should be addressed prior to publication. Specific comments are provided below.

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.

Abstract: The accuracy, time resolution and limit of detection (and corresponding integration time) should be clearly stated in the abstract.

The estimated limit of detection is already stated in the abstract (line 5). The integration time (5 minutes) has now been added. By propagating the uncertainties in the determination of the residence time (which depend on the uncertainty of the NO+O₃ reaction kinetics and of the NO concentration), and in the ozone measurements, and by taking into account the typical variability of the ozone wall loss, we estimate the total uncertainty of the instrument to be about 32%, based on equations 5 and 6. Note however that both the uncertainty and the detection limit of the instrument are somewhat variable because they are affected by the loss of ozone on the reactor wall – this element has been incorporated (conservatively) in the uncertainty estimate (see discussion in Section 4.2). The following modifications were made to the abstract, to the conclusions and to Section 5.1:

Lines 5-6: changed to “and proved able to measure reactivities corresponding to $> 4.5 \times 10^{-5} \text{ s}^{-1}$ (at 5 minutes averaging time), with an estimated total uncertainty of $\sim 32\%$. Such reactivities correspond to >20 ppb of α -pinene or >150 ppb of isoprene in isolation”

Line 359: added “From Eq. 5 and Eq. 6, the total uncertainty of TORS can be estimated by propagating the uncertainties in the determination of the residence time (related to the uncertainty in the concentration of the NO cylinder and in the rate coefficient of the NO+O₃ reaction, Sect. 4.1), the uncertainty of the ozone monitors (Sect. 3.1) and the median variability of R(wall) during individual experiments (Sect. 4.2) at $\sim 32\%$.”

Lines 469-470: changed to “The TORS instrument was able to measure O₃ reactivities with BVOCs (R(O₃)) of $4.5\text{-}9.0 \times 10^{-5} \text{ s}^{-1}$ or more – with a residence time of 140 seconds, an averaging time of 5 minutes, and an estimated total uncertainty of $\sim 32\%$. These values correspond to 20-40 ppb of α -pinene, 150-300 ppb of isoprene or 160-320 ppt of β -caryophyllene.”

Page 1, line 16: Consider changing ‘atmosphere’ to ‘troposphere’.

Done.

Page 1, line 17 (and elsewhere): Provide the relevant wavelengths for the reaction.

Done.

Page 2, line 29: Change ‘. . . state and primarily reacts . . .’ to ‘. . . state which primarily reacts . . .’

Done.

Page 3, line 52: The statement 'all BVOCs are very reactive with both OH and O₃ . . .' is not really true. At the top of the page, methanol, CO and acetone are listed as significant BVOC emissions, none of which are very reactive with O₃.

Changed to "Most BVOCs are reactive with OH and many of them, such as isoprene, monoterpenes and sesquiterpenes, include double carbon bonds and therefore also react with O₃:"

Page 4, line 78: k_i is the bimolecular rate coefficient, not the pseudo-first-order rate coefficient.

Corrected.

Page 4, line 85: Note that measurements of HO₂ reactivity have also been reported (Miyazaki et al., Rev. Sci. Instr., 84, 7, doi.10.1063/1.4812634).

The reference has been added.

Page 4, line 88: Are there other considerations for long-lived species? Is it necessary to assume that O₃ is in steady state?

No, unless the other long-lived species also react with O₃, in which case they contribute to the total reactivity in both the ambient atmosphere and the measurement. Equation 4 does not assume that O₃ is in steady-state.

Page 4, line 97: Consider changing 'when photolysis is zero' to 'when photolysis rates are zero'.

Done.

Page 4, line 99: The comparisons between RO₃ resulting from NO₂, alpha-pinene and limonene are a little confusing. If NO₂ has the lower rate coefficient it should require a greater concentration to reach the same O₃ reactivity as alpha-pinene or limonene. For the rate coefficients given in Table 1, and assuming T = 298 K, p = 1 atm, 1 ppb of NO₃ has RO₃ = 8.7e-7 s⁻¹, 2.7 ppb of alpha-pinene has RO₃ = 6.4e-6 s⁻¹ and 6.2 ppb of limonene has RO₃ = 3.4e-5 s⁻¹. Should this read that 2.7 ppb of NO₂ has the same RO₃ as 1 ppb of alpha-pinene and 6.2 ppb of NO₂ has the same RO₃ as 1 ppb of limonene? Please clarify.

We thank the reviewer for spotting this error which has been corrected. The sentence has been changed to: "1 ppb of NO₂ has the same O₃ reactivity as 0.37 ppb of a-pinene and 0.16 ppb of limonene (at 298 K)"

Page 5, line 127: The previous study describing measurements of RO₃ defines it as the total O₃ reactivity, and in their experiments/measurements assume [NO] = 0 and all observed RO₃ is a result of reactions with VOCs. In this case, where NO is present and its effects on the observed RO₃ has to be subtracted to give the O₃-VOC reactivity, would it be sensible to define this as a separate parameter to RO₃ where the O₃-NO reactivity is known? This would avoid any future confusion between studies that may define RO₃ as the total observed reactivity (as in the previous work) or as the subset of RO₃ owing to O₃-VOC reactivity (as in the current work).

The referee raises an issue which we considered carefully in adopting the definitions of ozone reactivity for this paper. The definition of R(O₃) used here is consistent with the definition used in previous studies (Matsumoto, 2014 & 2016). We define R(O₃) as the ozone reactivity due to BVOCs, and R(NO) as the ozone reactivity due to NO (see Eq. 6 on page 5). In the case of the previous studies, which were conducted in zero air, R(NO) = zero and the values of R(O₃) are therefore comparable.

The following sentence has been added to Line 129: "This definition of R(O₃) is directly comparable to the definition by Matsumoto (2014, 2016), since those experiments were conducted in zero air (i.e., at R(NO) = 0)."

Page 6, line 149: Please quantify the statement 'not substantially different'.

The difference between the model results is less than 0.1%. The number has been added to the text.

Page 7, line 169: Spelling of 'independent'.

Corrected.

Page 8, line 210: Please provide some further details regarding the requirements for the residence time. What difference in [O₃] is required for accurate measurements of ozone reactivity? How much change in [VOC] is acceptable before the measurement of ozone reactivity is affected?

The required difference in O₃ concentrations is not a fixed parameter, but depends on the BVOC loading. For the experiments described in this paper the drop in ozone concentration was typically of the order of a few ppb. We note however that the ratio between the two ozone measurements (before and after the reactor) is the more important quantity, as per Equation 5. The change in BVOCs must be such that pseudo first-order conditions are maintained for the duration of the residence time in the reactor. This is quantitatively discussed in Section 2.3 (lines 163-170).

Page 8, line 224: There is no hyphen in 'ad hoc' (also similar comments for in situ, 2 sigma, elsewhere).

Corrected.

Page 9, line 224: Please provide details of the mass transmission curve. What is the source? How does it affect the uncertainties in the measurements? What are the limits of detection for the VOC measurements?

We used the TO-14A aromatics standard mixture calibration gas and zero air to generate the mass transmission curve. The main uncertainty is that we are assuming that any compounds of interest that were not included in the mass transmission curve obey the same reaction kinetics in the reaction tube as the calibrated compounds. Holzinger et al. (2019) reported that a PTR-MS operated under standard conditions is able to accurately measure the concentration of uncalibrated compounds (to within 30%) if these compounds have high proton affinity and do not undergo unknown fragmentation using a mass transmission curve. This assumption is likely valid for BVOCs such as isoprene and monoterpenes (α-pinene and 3-carene), which were the primary focus during the laboratory plant experiments. Therefore based on the work by Holzinger et al., (2019), we are reasonably confident that we could quantify BVOCs levels, as we operated the PTR-MS using standard conditions (E/N of 129 Td). The reaction rate of many monoterpenes with H₃O⁺ are well-known and we used the reaction rate for α-pinene (2.04e9 cm³ s⁻¹ molecule⁻¹) as this was expected to be a major constituent for the lemongrass bag experiments. For the compounds that were included in the calibration gas, the limits of detection were calculated to be between 20-80 ppt, within the expected range (Sulzer et al. 2014). We assume that for BVOCs it is similar.

To clarify the calibration procedure using the mass transmission curve, we have amended the text between lines 231 and 236 as follows:

“The instrument (Sulzer et al., 2014) was operated according to the standard operating conditions recommended by the manufacturer (drift pressure = 3.8 mbar, drift tube temperature = 80 C and E/N = 129 Td), using H₃O⁺ as the reagent ion. Calibration was performed using a TO-14A aromatics standard mixture (Airgas Inc., USA). This mixture does not contain biogenic compounds, so a mass transmission curve calculated using the calibration gas was used for quantification. Recent work by Holzinger et al. (2019) showed that a PTR-MS operated under standard conditions is able to accurately measure concentration of uncalibrated compounds (to within 30%) using a mass transmission curve, if these compounds have high proton affinity and do not undergo unknown fragmentation. This assumption is likely valid for BVOCs such as isoprene and monoterpenes (Holzinger et al., 2019), which were the primary focus of this work. The limits of detection determined using zero air for calibrated compounds were in the order of 20-80 ppt.”

Page 9, line 259: What is ‘easy’ about detecting the peak at m/z 59? Mass separation from other peaks? Peak height/ionisation cross-section for acetone compared to other compounds?

We chose acetone for these experiments as it is easily ionised by H₃O⁺ ion and does not undergo fragmentation. Therefore it is straightforward to detect it by PTR-MS. To clarify the above, we have changed the text to read (line 258):

“Acetone was used as a tracer for these experiments because it is easily ionised by H₃O⁺ and does not undergo fragmentation, and consequently is straightforward to detect by PTR-MS at its protonated mass (m/z 59)”

Page 10, line 261 onwards: What is the flow regime in the instrument? Is the assumption of plug flow appropriate? How was the concentration of NO determined in method 2?

We have assumed a plug flow inside the reactor (lines 268-269) only for the calculation with Method 3. The other two methods do not make this assumption, but implicitly take into account the flow regime in the reactor. The NO concentration was known (with an uncertainty of 5%), because we used a certified cylinder for those experiments. Line 265 has been modified as follows:

“Method 2 uses the TORS technique to measure the reactivity of O₃ (~20 ppb) with NO: the sample flow contained only ~100 ppb of NO (diluted from a certified gas cylinder, 4.90 +/- 0.25 ppm in N₂, by BOC UK) and, since the rate coefficient of NO + O₃ is known (1.89e-14 cm³ molecule⁻¹ s⁻¹ at 298 K, with an uncertainty of 17% (Atkinson et al., 2004), the only unknown variable in Eq. 5 was the reaction time t.”

Page 10, line 292: Please quantify the ‘small but noticeable dependence of R_{wall} on humidity’.

The sentence has been changed to: “R_{wall} showed a weak dependence on the relative humidity inside the reactor (R_{wall} = 9.6e-7* RH + 4.4e-5, with R² = 0.198)”

On line 298 “no observable pattern” was changed to “no clear pattern”.

Page 11, line 295: State the temperature range in the text.

Added.

Page 11, line 298 onwards: What is the standard deviation and median of the measured ozone wall loss? Can the limit of detection be quantified more precisely using the observed variability in the ozone wall loss?

The median and the average standard deviation of the ozone wall loss have been added to the text. The standard deviation is variable within the same experiment and from experiment

to experiment (see Figure 5), which means that the detection limit is also variable (Equation 6). The average standard deviation of the ozone wall loss ($2.4 \times 10^{-5} \text{ s}^{-1}$) corresponds to a reactivity of ~ 10 ppb of α -pinene. As indicated in Section 5.1 (lines 350-351), below 10 ppb the measured reactivities are statistically indistinguishable, but since the wall loss can be higher than that, the estimated detection limit can also be larger. The following changes were made to the manuscript:

Lines 300-301: "The average standard deviation of $R(\text{wall})$ was $2.4 \times 10^{-5} \text{ s}^{-1}$ and the interquartile range was $0.5\text{-}1.2 \times 10^{-4} \text{ s}^{-1}$ (mean = $9.8 \times 10^{-5} \text{ s}^{-1}$, median = $7.1 \times 10^{-5} \text{ s}^{-1}$), which corresponds..."

Page 11, line 311: Please provide further details of the experiments that led to '... eventually settling on a sample flow of ~ 2.3 slpm'. What were the ranges of conditions investigated? How did the instrument perform under these conditions? Why was a flow of ~ 2.3 slpm considered optimum?

We experimented with several values of the ozone flow between 500 and 2500 sccm. The sample flow was adjusted accordingly, so that all the flows of the system were balanced. We settled on a combinations of flows which worked well with the conditions we had in the laboratory experiments, but we recognize that not all the possible combinations of flows have been explored. Therefore it is not possible to say that these are the absolute optimum settings for the system. This is indeed one of the objectives of the future work on the instrument, as indicated in the Conclusions.

Page 11, line 323: What is the impact of the difference of ~ 1 ppb on the uncertainty in the ozone reactivity measurements?

There is no impact. As mentioned on lines 321-322, we apply a correction factor to the ozone data to account for the difference between the monitors.

Page 12, line 345: How well did the concentrations determined from the diffusion tubes agree with those determined by the PTR-MS measurements?

The agreement was, on average, within 14%. The text has been modified as follows:

"The concentration of α -pinene was then calculated from the diffusion rate and confirmed via direct measurements by PTR-MS (Sect. 3.2) with an agreement of $\sim 14\%$."

Page 12, line 348: Please quantify 'reasonable agreement'.

The sentence has been changed to "The agreement between the calculated and measured ozone reactivity for α -pinene mixing ratios larger than 40 ppb was about 25% -- within the combined uncertainties of the instrument and of the α -pinene + O₃ rate coefficient (41%, Atkinson et al. (2004))"

Page 12, line 358: The range of values for the limit of detection are 1/3 to 2/3 of that described previously, 'comparable' is somewhat subjective. How does the residence time affect this? A more detailed description of the instrument used in previous studies would be helpful to provide the reader with a more informed comparison.

A detailed description of the instrument used in previous studies is beyond the scope of this paper, but can be found in Matsumoto (2014). The observed ozone change is inversely proportional to the residence time (see Equation 5), and therefore the instrument detection limit also is inversely proportional to the residence time (subject to the limitations in the consumption of BVOCs in order to maintain pseudo first-order conditions). Therefore, if the residence times of the two instruments differ by a factor of about 2, the corresponding detection limits can be expected to vary by roughly the same amount.

Page 13, lines 372-375: What were the sources of the Teflon bag, halogen lamp and small fan?

Added.

Page 13, line 376: What is meant by 'the natural humidity of the plants'? Natural release of water vapour via transpiration and evaporation by the plants?

That is correct. The sentence has been modified as suggested.

Page 13, line 383: What are the uncertainties in the stated values?

Given the variability of the data (Figure 7) it makes more sense to state the interquartile range, because the standard deviation of the timeseries would be of the same order of magnitude of the mean. We refer to Section 5.1 for a discussion of the instrumental uncertainties (see above).

Page 14, line 408: Please provide some approximate quantification for the statement 'concentrations of BVOCs . . . are higher and the concentrations of NO lower . . .'. Page 15, line 458: What is the basis for the assumption of NO in the reactor being ~20% of the ambient concentration?

Given the location of the experiment– a suburban area in central England – we feel that it is reasonable to assume that the levels of BVOCs inside the glasshouse were higher than in the nearby environment. Unfortunately, we cannot be quantitative in the absence of simultaneous measurements of BVOCs inside and outside the glasshouse.

As for the issue of NO levels inside the glasshouse and related discussion we have decided to remove this section and Figure 9 from the paper. Please see the extended discussion in our reply to reviewer #2.

Page 14, line 415: What was the variability in the measured wall loss?

The following was added to the text: "The ozone wall loss during the measurement period varied between $4.9e-5$ and $1.1 e-4$ s⁻¹ (first and third quartiles), with mean values between $0.7e-4$ and $1.1e-4$ s⁻¹."

Page 14, line 420: What were the most important species?

This information is on the following page (lines 432-433).

Page 14, lines 422 and 423: What are the uncertainties in the stated means?

Given the variability of the data (Figure 8) it makes more sense to state the interquartile range, because the standard deviation of the timeseries would be of the same order of magnitude of the mean. We refer to Section 5.1 for a discussion of the instrumental uncertainties (see above).

Page 15, line 449: Change '. . . ozone reactivity tends peak . .' to '. . . ozone reactivity tends to peak . .'

Done.

Page 16, line 476: It's not clear how the listed improvements will be achieved or how TORS will be able to make ambient measurements (line 479). Specific details would help to avoid this simply reading as a wishlist.

The paragraph is intended to highlight the areas of future development for the TORS technique. It also provides guidelines for other researchers that may be considering using this approach. We have changed to text as follows:

Line 476: "Further work will improve" changed to "Further work will aim to improve"

Line 478-479: "In the future, TORS will be able" changed to "With these improvements and proper supporting measurements, the detection limit and the uncertainty of TORS can be improved and the technique will be able to make measurements under a wider range of conditions"

Also, for consistency, the following changes were made to the abstract and the conclusions:

Lines 6-7: changed to "larger than typical ambient levels, but observable in environmental chamber and enclosure experiments, as well as in BVOCs-rich environments"

Lines 470-472: changed to "These mixing ratios are larger than typical ambient levels, but can be observed in BVOCs-rich forested environments and in enclosure studies (Duhl et al., 2008; Bouvier-Brown et al., 2009, Kammer et al., 2018), and can easily be reproduced in laboratory and environmental chamber experiments."