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 > 4.5e-5 s-1 (at 5 minutes averaging time), with an estimated total uncertainty of ~32%. Such reactivities correspond to >20 ppb of a-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 ~32%.”

Lines 469-470: changed to “The TORS instrument was able to measure O3 reactivities with BVOCs (R(O3)) of 4.5-9.0e-5 s-1 or more – with a residence time of 140 seconds, an averaging time of 5 minutes, and an estimated total uncertainty of ~32%. These values correspond to 20-40 ppb of a-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: ki 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 (a-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 a-pinene (2.04e9 cm3 s-1 molecule-1) as this was expected to be a major constituent for the lemonthyme 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.

The 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 we 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 Rwall on humidity’.

The sentence has been changed to: “Rwall showed a weak dependence on the relative humidity inside the reactor (Rwall = 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 (2.4e-5 s-1) corresponds to a reactivity of ~10 ppb of a-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(wall) was 2.4e-5 s-1 and the interquartile range was 0.5-1.2e-4 s-1 (mean = 9.8e-5 s-1 , median = 7.1e-5 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 a-pinene was then calculated from the diffusion rate and confirmed via direct measurements by PTR-MS (Sect. 3.2) with an agreement of ∼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 a-pinene mixing ratios larger than 40 ppb was about 25% -- within the combined uncertainties of the instrument and of the a-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."

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 1.3e6 and 4e6 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 a-pinene <5 ppb) and 10 ppm (for a-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 a-pinene (Fig. 1a-c), at least within the range of a-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[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.

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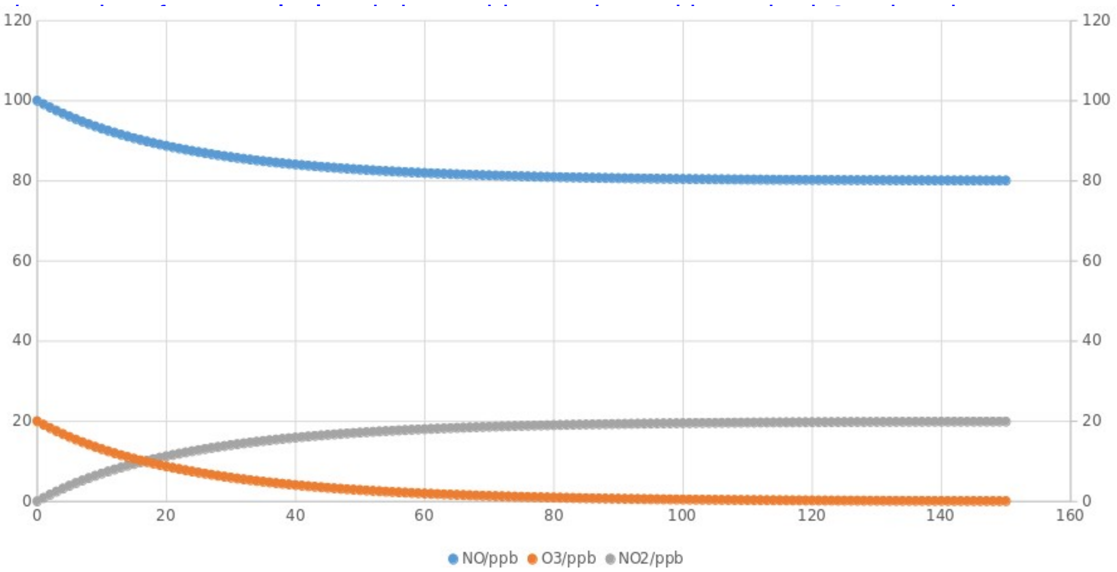

Lines 274-275: changed to “In the experiments described in Sect. 5, we used a value of 140 seconds for the residence time, determined by fitting a 2nd degree polynomial to all three methods, as shown in Fig. 4b for a reactor flow of 2470 sccm.”

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[NO] = 0.04 (s-1?), -LN(O3(t)/O3(0)) is about 4, and the slope of the regression line is roughly found as 4/0.04 ∼ 100 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 x 10ˆ-14, [O3] (30 ppb) is about 7.5x10ˆ11, then k[O3] is about 1.5x10ˆ-2 s-1. Thus, the lifetime of NO is about 67 sec (= 1/(1.5x10ˆ-2 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 NOx & low NO’ ? Please clarify the conditions.

The reviewer is correct that high NOx 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 NOx conditions, not for laboratory, enclosure and environmental chamber experiments under low or zero NOx 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 O3 = 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.

An instrument for in situ measurement of total ozone reactivity

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Abstract. We present an instrument for the measurement of total ozone reactivity – the reciprocal of the chemical lifetime of ozone (O_3) – in the troposphere. The Total Ozone Reactivity System (TORS) was developed with the objective to study the role of biogenic volatile organic compounds (BVOCs) as chemical sinks of tropospheric ozone. The instrument was extensively characterized and tested in the laboratory using individual BVOCs and small plants (lemonthyme, *Thymus citriodorus*) in a Teflon bag and proved able to measure reactivities corresponding to $> 4.5 \times 10^{-5}\ \mathrm{s}^{-1}$ (at 5 minutes averaging time), with an estimated total uncertainty of ∼32%. Such reactivities correspond to >20 ppb of α-pinene or >150 ppb of isoprene in isolation – larger than typical ambient levels, but observable in environmental chamber and enclosure experiments, as well as in BVOC-rich environments. The functionality of TORS was demonstrated in quasi-ambient conditions with a deployment in a horticultural glasshouse containing a range of aromatic plants. The measurements of total ozone reactivity made in the glasshouse showed a clear diurnal pattern, following the emissions of BVOCs, and is consistent with mixing ratios of tens ppb of monoterpenes and several ppb of sesquiterpenes.

1 Introduction

Ozone (O_3) is a key component of the troposphere: it is known to be damaging for human health and vegetation, to reduce crop yields, and it is an important greenhouse gas (Monks et al., 2015). Ozone is also a primary source of the OH radical, the main atmospheric oxidant, and acts as an oxidant itself (Johnson and Marston, 2008). Because of its importance to tropospheric chemistry, the ozone budget has long been a subject of considerable interest. Ozone is not directly emitted, but is formed in the troposphere via photolysis of nitrogen dioxide (NO_2), followed by reaction of atomic oxygen with molecular oxygen (R1-R2):

$$\mathrm{NO_2 + h\nu \rightarrow O(^3P) + NO} \qquad (\lambda < 420\ \mathrm{nm}) \tag{R1}$$

$$\mathrm{O(^3P) + O_2 + M \rightarrow O_3 + M} \tag{R2}$$

Ozone is destroyed in the troposphere via a series of processes, both physical (e.g., dry and wet deposition) and chemical (Monks et al., 2015). The latter involve photolysis (R3-R4) and reactions with a range of inorganic molecules and unsaturated volatile organic compounds (R5-R9):

$$\mathrm{O_3 + h\nu \rightarrow O(^3P) + O_2} \qquad (\lambda < 340\ \mathrm{nm}) \tag{R3}$$

$$\mathrm{O_3 + h\nu \rightarrow O(^1D) + O_2} \qquad (\lambda < 340\ \mathrm{nm}) \tag{R4}$$

$$\mathrm{O_3 + NO \rightarrow NO_2 + O_2} \tag{R5}$$

$$\mathrm{O_3 + NO_2 \rightarrow NO_3 + O_2} \tag{R6}$$

$$\mathrm{O_3 + OH \rightarrow HO_2 + O_2} \tag{R7}$$

$$\mathrm{O_3 + HO_2 \rightarrow OH + 2O_2} \tag{R8}$$

$$\mathrm{O_3 + unsaturated\ VOCs \rightarrow products} \tag{R9}$$

Ozone photolysis forms atomic oxygen in ground $(\mathrm{O(^3P)})$ and excited $(\mathrm{O(^1D)})$ states, which primarily react with molecular oxygen in the atmosphere to reform ozone in a null cycle (R2, R10). However, a small fraction (∼10% in the lower troposphere) of $\mathrm{O(^1D)}$ reacts with water vapour to form OH radicals (R11), a key process for the oxidative capacity of the atmosphere:

$$\mathrm{O(^1D) + O_2 + M \rightarrow O_3 + M} \tag{R10}$$

$$\mathrm{O(^1D) + H_2O \rightarrow 2OH} \tag{R11}$$

The chemical losses of ozone are one of the least understood parts of the tropospheric ozone budget, in particular because of the many unknowns related to the abundance of volatile organic compounds (VOCs) and their reactivity with ozone (Johnson and Marston, 2008; Glasius and Goldstein, 2016). The organic compounds that react with ozone contain one or more double carbon bonds (e.g., alkenes and dialkenes), and many of these species are emitted by plants during their metabolic processes. These biogenic VOCs (BVOCs) constitute a large fraction of the carbon loading of the atmosphere: estimates suggest that the total biogenic sources of VOCs can be 8-10 times larger than the total anthropogenic sources (Williams, 2004; Glasius and Goldstein, 2016). Isoprene is by far the most important reactive BVOC, accounting for $\sim$50% of the total natural emissions of non-methane hydrocarbons by mass, followed by monoterpenes (15%), methanol (9%), CO (7%) and a range of other organic compounds which include acetone (4%) and sesquiterpenes (3%) (Guenther et al., 2012).

However, due to the limitations of the analytical techniques used to measure VOCs, it is very likely that both the number and the mass of BVOCs in the troposphere are severely underestimated (Di Carlo et al., 2004; Sinha et al., 2010; Whalley et al., 2011). Estimates vary depending on the approach used, but it is thought that between 20% and 60% (and possibly more) of the total organic carbon pool in the troposphere is currently unaccounted for (Lewis et al., 2000; Goldstein and Galbally, 2007; Glasius and Goldstein, 2016). A significant fraction of these unmeasured organic compounds is constituted by biogenic VOCs: besides isoprene, only a few monoterpenes (e.g., α-pinene, β-pinene, limonene) and even fewer sesquiterpenes (e.g., β-caryophyllene) are routinely measured in the atmosphere (Bouvier-Brown et al., 2009; Hellén et al., 2018). Sesquiterpenes are particularly challenging to measure, due to their low vapour pressure, and therefore their ambient levels are most likely underestimated (Pollmann et al., 2005; Duhl et al., 2008; Kim et al., 2009).

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 O_3: therefore, the existence of a significant pool of unknown and unmeasured BVOCs has important consequences for the quantification of the ozone budget, which is crucial to understand the environmental and societal impacts of ozone pollution. The oxidation of BVOCs by ozone is especially important because it forms additional pollutants, such as secondary organic aerosol, and impacts key chemical processes, such as the conversion of NO to NO_2 and therefore the formation of ozone via R1-R2, as well as the radical budget (Lewis et al., 2000; Glasius and Goldstein, 2016). Missing a large fraction of BVOCs means that all these processes remain potentially underestimated.

One way to address this problem is to expand the number of VOCs that can be measured. This approach has achieved some success, thanks to comprehensive 2-dimensional gas chromatographic techniques (Pankow et al., 2012; Edwards et al., 2013; Glasius and Goldstein, 2016). However, the chemical complexity of the composition of ambient air makes it difficult, if not impossible, to completely quantify the VOC loading of the atmosphere. An alternative approach is to measure an integrated chemical property of all VOCs, such as the chemical lifetime, which includes all the reactions that remove a given species, in this case O_3 (R3-R9). Instruments to directly measure the total ozone reactivity have been demonstrated by Park et al. (2013) and Matsumoto (2011, 2014), and used for laboratory studies of gas-phase ozonolysis reactions (Matsumoto, 2016).

This paper presents an instrument designed to measure total ozone reactivity under ambient, environmental chamber and branch enclosure conditions. The Total Ozone Reactivity System (TORS) was developed from the instrument described by Matsumoto (2014) with several modifications, as described below. Section 2 describes the theoretical and operating principles of TORS, while Sect. 3 and Sect. 4 describe the design and the laboratory characterization of the TORS instrument, respectively. In Sect. 5 the TORS instrument is evaluated with three types of experiments, increasingly approaching ambient conditions:

laboratory measurements with known concentrations of selected BVOCs, laboratory measurements with small plants, and quasi-ambient measurements in a horticultural glasshouse.

2 Ozone Reactivity

2.1 Reactivity measurements

The atmospheric lifetime (τ) of a generic species A is defined as the inverse of its total chemical loss rate, i.e. of its chemical reactivity (R):

$$\tau_{(A)} = \frac{1}{R_{(A)}} = \frac{1}{\Sigma_i k_i [\mathrm{X}]_i} \tag{1}$$

where $[\mathrm{X}]_i$ is the concentration of a molecule reacting with A and k_i is the corresponding bimolecular rate coefficient. The chemical lifetime of a species has long been considered a useful diagnostic parameter, especially to investigate the loss terms of key atmospheric oxidants, such as the OH radical, which are generally less well known than the respective production terms (Bell et al., 2003).

The comparison between the directly measured lifetime and the lifetime calculated from an independent determination of k_i and $[\mathrm{X}]_i$ (Eq. 1) allows us to understand whether all the loss terms for a given species have been accounted for. This approach has been used with success to investigate the budget of the OH radical (Kovacs and Brune, 2001; Ingham et al., 2009; Sinha et al., 2010; Whalley et al., 2016; Fuchs et al., 2017; Sanchez et al., 2018), of the $\mathrm{HO_2}$ radical (Miyazaki et al., 2013) and of the $\mathrm{NO_3}$ radical (Sobanski et al., 2016; Liebmann et al., 2018). Measurements of OH reactivity have also helped to discover previously unknown chemistry in terms of recycling and losses of the OH radical (Di Carlo et al., 2004; Lou et al., 2010; Whalley et al., 2011).

The same principle can be used to investigate the chemical loss of ozone. From reactions R1-R11, the rate of production/loss of tropospheric ozone can be calculated as:

$$\frac{d[\mathrm{O_3}]}{dt} = -(k_{\mathrm{NO}}[\mathrm{NO}] + k_{\mathrm{NO2}}[\mathrm{NO_2}] + k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{HO2}}[\mathrm{HO_2}] + \Sigma_i k_i [\mathrm{VOC}]_i)[\mathrm{O_3}] - \alpha j_{\mathrm{O3}}[\mathrm{O_3}] + j_{\mathrm{NO2}}[\mathrm{NO_2}] \tag{2}$$

where α is the fraction of atomic oxygen that does not reform $\mathrm{O_3}$ via reaction with $\mathrm{O_2}$ (R11). Halogens (X = Cl, Br, I) can also react with ozone to form halogen oxides (XO), although this process is likely minor in continental environments far from the main halogen sources (Monks et al., 2015; Simpson et al., 2015). Under the typical unpolluted conditions that can be encountered in a forested environment (NO = 50 ppt, $\mathrm{NO_2}$ = 500 ppt, OH = 5×10^6 molecule cm^{-3}, $\mathrm{HO_2}$ = 1×10^8 molecule cm^{-3}, Griffith et al. (2013)), the loss of ozone to $\mathrm{NO_2}$, OH and $\mathrm{HO_2}$ is a factor of 50-100 times slower than the loss of ozone to NO (Table 1). Under more polluted conditions, $\mathrm{NO_2}$, OH and $\mathrm{HO_2}$ reactions are even less important as ozone sinks compared to NO.

During the night – when photolysis rates are zero, and the concentrations of OH and HO_2 are typically 2 orders of magnitude lower than during the day – NO is titrated to NO_2 (R5) soon after sunset, leading to the formation of NO_3 radicals (R6). The rate coefficient of O_3 + NO_2 is small ($k = 3.52 \times 10^{-17}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, Table 1) compared to the rate coefficients of most monoterpenes and sesquiterpenes with O_3 (since its emissions are light dependent, isoprene is normally not present at night (Guenther et al., 2012)): for example, 1 ppb of NO_2 has the same O_3 reactivity as 0.37 ppb of α-pinene and 0.16 ppb of limonene (at 298 K). This means that NO_2 can be a significant ozone loss during the night if its concentration is high – which is not usually the case in unpolluted forested environments. Equation 2 can thus be simplified to:

$$\frac{d[\mathrm{O_3}]}{dt} = -(k_{\mathrm{NO}}[\mathrm{NO}] + k_{\mathrm{NO2}}[\mathrm{NO_2}] + \Sigma_i k_i[\mathrm{VOC}]_i)[\mathrm{O_3}] - \alpha j_{\mathrm{O3}}[\mathrm{O_3}] + j_{\mathrm{NO2}}[\mathrm{NO_2}] \tag{3}$$

where the NO and photolysis terms are significant only during the day and the NO_2 term is significant only during the night (and under relatively high NO_x conditions). The concentrations of O_3, NO and NO_2, their rate coefficients with O_3 and the photolysis rates of O_3 and NO_2 can be measured and/or are well known. Therefore, Eq. 3 can be used to evaluate the contribution of the volatile organic compounds ($\Sigma_i k_i[\mathrm{VOC}]_i$). As mentioned in Sect. 1, only a handful of the VOCs that react with ozone are routinely measured, which likely leads to underestimation of the VOC contribution to ozone loss. If the loss rate of ozone can be directly measured, it is possible to determine the total VOC loading and compare it with the measured VOCs, thus allowing an estimate of missing (i.e., non measured) VOCs.

2.2 TORS concept

The Total Ozone Reactivity System (TORS) is based on the technique developed by Matsumoto (2014). At its core, the system is a dark flow tube reactor in which a known amount of ozone is reacted with a sample (e.g., NO, unsaturated VOCs). If the change in the concentration of the co-reactants in the sample is small, the reaction follows pseudo first-order kinetics and the change in ozone concentration is described by:

$$[\mathrm{O_3}]_t = [\mathrm{O_3}]_0 \times e^{-k't} \tag{4}$$

where $[\mathrm{O_3}]_0$ and $[\mathrm{O_3}]_t$ are, respectively, the initial and final ozone concentrations, k' is the pseudo first-order rate coefficient and t is the reaction time, which corresponds to the reactor residence time and can be determined experimentally (Sect. 4.1). Equation 4 can be solved analytically provided the reaction time and the initial and final O_3 concentrations are known:

$$k' = \frac{-ln([\mathrm{O_3}]_t/[\mathrm{O_3}]_0)}{t} \tag{5}$$

TORS provides a direct measurement of k', which includes the chemical reactions inside the reactor (described by Eq. 3) plus other O_3 removal processes, such as the loss of ozone on the reactor wall. Since the reactor is completely dark, the photolysis terms in Eq. 3 can be neglected and the only contributors to the O_3 chemical loss are NO and VOCs. The focus of this study is on the reactivity of VOCs (Sect. 1), and therefore the loss of O_3 due to NO and to the reactor wall need to be subtracted. For the purpose of this work, we define ozone reactivity (R_{O3}) as:

$$R_{O3} = k' - R_{NO} - R_{wall} = k' - k_{NO}[NO] - R_{wall} = \Sigma_i k_i [VOC]_i \tag{6}$$

where R_{NO} is the removal of O_3 by reaction with NO and R_{wall} is the loss of O_3 on the reactor wall. 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). The ozone loss on the reactor wall (R_{wall}) is a potentially significant parameter in the TORS technique and requires accurate and precise determination (Sect. 4.2). Another potentially important factor is the effect of secondary reactions, which can increase the loss of ozone (R5-R8) causing overestimation of R_{O3} or can decrease the concentration of VOCs in the sample via reactions other than ozonolysis (e.g., if there is significant formation of NO_3 in the reactor via R6) causing underestimation of R_{O3}.

Particularly important can be the formation of OH radicals from VOC ozonolysis (Paulson et al., 1999; Rickard et al., 1999; Johnson and Marston, 2008): to remove this interference, an OH scrubber, such as cyclohexane, can be added to the system. Cyclohexane does not react with O_3, but reacts quickly with OH ($k = 6.95 \times 10^{-12}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$) and forms organic peroxy radicals which combine with HO_2 to form products that do not react with O_3 (Alam et al., 2011). Therefore, cyclohexane acts as an efficient OH scrubber when present at high mixing ratios (ppm level). The effects of the ozone wall loss and of the secondary chemistry of ozonolysis products were investigated with a box-model simulation of the TORS chemistry (Sect. 2.3) and with laboratory characterization experiments (Sect. 4.2).

2.3 Simulation of TORS chemistry

A box-model was used to simulate the chemical reactions occurring in the TORS reactor. The main objective of the model was to assess the effect of the OH radicals generated by the ozonolysis of VOCs and the role of the OH scrubber, as well as the impact of potential interfering chemistry such as removal of ozone by OH, HO_2 and NO_2 (R6-R8), and removal of VOCs by OH and NO_3 radicals.

The model was assembled using the AtChem2 modelling toolkit (Sommariva et al., 2019) with the inorganic chemistry and the oxidation mechanisms of α-pinene and cyclohexane taken from the Master Chemical Mechanism (MCM v3.3.1, Saunders et al. (2003)). The cyclohexane mechanism was updated to include a more accurate representation of the ring-opening path of the cyclohexoxy radical, following Alam et al. (2011), although the model results were not subtantially different from those of a model using the MCM standard cyclohexoxy radical scheme ($\leq$0.1%). It must be noted that the model results depend on the VOC used, as the OH yield from ozone + alkene reactions can vary from 0.16 for ethene to 0.90 for 2,3-dimethyl-2-butene (Johnson and Marston, 2008). The choice of α-pinene for the model, as well as for the laboratory experiments (Sect. 5.1) is due to the fact that α-pinene is one of the most abundant BVOC (Guenther et al., 2012). It also has a high OH yield (0.8, Johnson and Marston (2008)), allowing an estimate of the upper bounds of the the potential interferences caused by OH chemistry.

The model was initialized with a range of α-pinene mixing ratios (0.1-50 ppb) and, for each, with a range of cyclohexane mixing ratios (0-20 ppm). The initial mixing ratios of NO and NO_2 were 50 and 500 ppt, respectively, representative of an unpolluted forested environment (Griffith et al., 2013). The initial O_3 mixing ratio was set to 120 ppb, as used during the experimental work (Sect. 4.3). The model runtime was 300 seconds, covering the range of potential instrument residence times (Sect. 4.1). A summary of the model results is shown in Fig. 1.

The removal of α-pinene during the residence time in the reactor was $\sim$7% and 4-5% for initial α-pinene mixing ratios of 0.1 ppb and $\geq$0.5 ppb, respectively (Fig. 1a). In the absence of cyclohexane, the removal of α-pinene was slightly higher (1-2 percentage points) due to reaction with OH radicals. These numbers indicate that the consumption of α-pinene inside the reactor was over an order of magnitude smaller than its initial concentration and, therefore, the chemical system approached the pseudo first-order conditions required for the TORS method (Sect. 2.2). The error in the determination of ozone reactivity caused by the assumption of pseudo first-order conditions can be estimated at <4% for α-pinene mixing ratios >10 ppb. As expected (Alam et al., 2011), the reactions with oxidation products of cyclohexane were not significant sinks for ozone: apart from the wall loss, which is not included in the model, the loss of O_3 inside the reactor was less than 1.5% for α-pinene mixing ratios up to 50 ppb and was independent on the concentration of cyclohexane (Fig. 1b).

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 $\mathrm{molecule\,cm^{-3}}$ for α-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 level of cyclohexane above 10 ppm did not cause further significant 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. Figure 1d shows that the ozone reactivities determined with 1 and 20 ppm of cyclohexane were essentially the same for α-pinene initial mixing ratios up to 50 ppb. Moreover, the model results show that the differences between the ozone reactivity calculated with and without cyclohexane were between +1% and -6%, depending on the α-pinene level (Fig. 1d). This demonstrates that OH chemistry has a small overall impact on the determination of total ozone reactivity, a conclusion that is supported by the laboratory experiments (Sect. 5.1).

Model calculated HO_2 concentrations were less than 1×10^8 $\mathrm{molecule\,cm^{-3}}$, meaning that ozone reactivity with HO_2 was two orders of magnitude lower than ozone reactivity with α-pinene (at 10 ppb of α-pinene). Only at very low concentrations of α-pinene (<0.1 ppb) was HO_2 a significant sink for ozone. The presence of NO_3 radicals in the reactor is a potentially important interference for the TORS technique, both because its formation consumes O_3 (R6) and because NO_3 reacts quickly with α-pinene ($k = 6.2 \times 10^{-12}$ $\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$). Ambient NO_3 is likely lost in the inlet before the reactor, since the transmission of NO_3 through the inlet – a 6 mm diameter, 5 m long teflon tube with a residence time of $\sim$4 seconds – is poor (Dubé et al., 2006). However, NO_3 can be formed inside the reactor via R6 and the model calculated NO_3 formation of the order of 10^6 $\mathrm{molecule\,cm^{-3}}$ for α-pinene mixing ratios >5 ppb. Although the rate coefficient of α-pinene + NO_3 is 5 orders of magnitude larger than the rate coefficient of α-pinene + O_3, the ozone concentration in the reactor is 6-7 orders of magnitude higher than the concentration of NO_3. Therefore the reactivity of α-pinene with O_3 was 1-2 orders of magnitude larger than its reactivity with NO_3 (Table 1). It must also be noted that NO_3 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.

To summarize, the model of the TORS reactor suggest that, under the typical operating conditions described in Sect. 4.3, the concentrations of HO_2 and NO_3 are too small to compete with BVOCs for reaction with O_3. Additionally, the model provides no indication that the products of the oxidation of cyclohexane, when used as OH scrubber, can significantly affect the determination of total ozone reactivity. While ppm levels of cyclohexane effectively eliminate the OH radicals formed by BVOC ozonolysis reactions, the model suggests that ozone reactivities determined with and without an OH scrubber differ by $<6\%$. The model results are in agreement with the discussion in Sect. 2.1, where it was concluded that the decay of O_3 in the TORS reactor is predominantly due to the reactions with NO and VOCs, alongside loss on the reactor wall (Eq. 6). It is important to note, however, that the conclusions drawn from the model simulations may vary depending on the chemical conditions in the reactor, as several factors affect the chemistry inside the TORS reactors: the type and mixture of VOCs in the sample, their OH yields, the ambient concentrations of NO and NO_2 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.

3 Instrumentation

3.1 Description of TORS

The operating principles of TORS are described in Sect. 2.1 and Sect. 2.2, and a diagram of the TORS instrument is shown in Fig. 2. The reactor is a 1 m long polytetrafluoroethylene (PTFE) tube with an external diameter of 90 mm and an internal diameter of 87.33 mm. Several different materials and geometries for the reactor were tested during the instrument development phase and this design was found to allow a residence time inside the reactor sufficient for the ozonolysis reactions to take place to a suitably measurable extent, while minimizing the consumption of VOCs – in order to maintain pseudo-first order conditions – and the loss of ozone on the reactor wall (Sect. 4.1).

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). The ozone flow is mixed with the sample flow just before the reactor and the initial ozone concentration ($[O_3]_0$) is measured at this point, while the final ozone concentration ($[O_3]_t$) is measured at the exit point of the reactor (Fig. 2). Depending on the instrument settings, this setup produces an O_3 mixing ratio in the reactor of 100-140 ppb. Ozone concentrations are measured using two identical UV photometric O_3 monitors (Model 49i, Thermo Fisher Scientific, USA). The Model 49i O_3 monitor has a stated detection limit of 1 ppb and a precision of 0.25 ppb at 1 minute averaging time. The reactor can be bypassed using two 3-way teflon valves, so that the two ozone monitors can simultaneously measure the O_3 concentration before it enters the the reactor, thus allowing the ozone measurements to be corrected for any difference between the two monitors (Sect. 4.3). In addition, a T/RH probe (HMP110, Vaisala Oyj, Finland) is inserted in the reactor to monitor temperature and relative humidity. All the flows in the

TORS instrument are controlled with mass flow controllers (Brooks Instrument LLC, USA) using a custom-built control box (IGI Systems Ltd, UK). The signals from the ozone monitors, the T/RH probe and the mass flow controllers are logged on a laptop and processed with bespoke software in the R programming language.

A potentially important factor for TORS is the stability of the ozone source: highly variable levels of O_3 in the ozone flow (Fig. 2) can affect the determination of the ozone reactivity and increase the signal-to-noise ratio of the instrument. The ozone mixing ratio generated by the mercury lamp was found to vary, on average, by 0.4-0.6 ppb (5 minutes, 2σ), i.e. less than 1%. The ozone reactivity measurements reported in Sect. 5 were all averaged to 5 minutes.

3.2 Supporting VOC measurements

A proton-transfer-reaction time-of-flight mass spectrometer (PTR-QiTOF-MS, Ionicon Analytik GmBH, Austria) was used to measure VOC concentrations during the laboratory experiments (Sect. 5.1 and Sect. 5.2). 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 $^\circ\mathrm{C}$ and E/N = 129 Td), using H_3O^+ 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.

Measurements of BVOCs can be problematic for monoterpenes and sesquiterpenes, as the PTR technique cannot distinguish between isomers (de Gouw and Warneke, 2007). Typically, when measured by PTR-MS the main fragment ions for monoterpenes and sesquiterpenes are at m/z 81.07 and 149.1, respectively, and this fragmentation is independent of the structure of the isomers (Tani et al., 2003; Kim et al., 2009). Therefore total monoterpene and sesquiterpene concentrations were estimated using the abundances of the protonated parent ions (m/z 137 and 205, respectively) and of the main fragment ions (m/z 81 and 149, respectively). Other compounds associated with biogenic emissions (e.g., substituted monoterpene alcohols, after loss of a neutral H_2O) can also be detected at these fragment ions (Kim et al., 2010) and thus the estimated concentrations shown here may be considered upper limits.

The PTR-MS instrument was not available for the experiments outside the laboratory (Sect. 5.3). Instead, samples were taken with adsorption tubes, which were desorbed using a TD Unity-2 thermal desorption unit (Markes Int., UK) and subsequently analyzed with a gas chromatograph (GC 7890B, Agilent Technologies, USA) interfaced with a BenchTOF-Select time-of-flight mass spectrometer with tandem ionisation (Markes Int., UK). Further information on the analytical technique and the GC protocol can be found in Alam et al. (2016). The GC-MS analysis were only qualitative due to unavailability of appropriate calibration standards, and the data were used to identify the VOCs in the samples.

4 Characterization of TORS

4.1 Residence time

The residence time is one of the key parameters in Eq. 5 and therefore needs to be determined as accurately as possible. The geometry of the reactor and the total flow (sample + ozone) affect the residence time. Three methods were used to determine the residence time: 1) direct measurement using a double injection of acetone 2) indirect measurement via determination of NO reactivity with O_3 and 3) calculation using the flow rate and the internal volume of reactor (5990 cm^3).

Method 1 is illustrated in Fig. 3: the reactor was connected to the PTR-MS and aliquots of 0.05 µl of acetone, in a flow of zero air, were injected simultaneously at the entrance and at the exit of the reactor. Acetone was used as a tracer for these experiments because it is easily ionised by H_3O^+ and does not undergo fragmentation, and consequently is straightforward to detect by PTR-MS at its protonated mass (m/z 59). The simplest way to determine the residence time is to measure the time lag between the detection of the first and the second acetone peak signals by the PTR-MS ("maxima" in Fig. 3). However, the flow dynamics inside the reactor are complex and, as a consequence, there is no single value of residence time, but a distribution (Cazorla and Brune, 2010; Huang, 2016). Hence, the acetone signal from each injection can also be used to determine the mean residence time in the reactor ("means" in Fig. 3): the residence times estimated using the "means" calculations are about 40% larger than those estimated using the "maxima" calculations.

Method 2 uses the TORS technique to measure the reactivity of O_3 ($\sim$20 ppb) with NO: the sample flow contained only $\sim$100 ppb of NO (diluted from a certified gas cylinder, 4.90 ± 0.25 ppm in N_2, by BOC UK) and, since the rate coefficient of NO + O_3 is known (1.89×10^{-14} $\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$ at 298 K, with an uncertainty of 17% (Atkinson et al., 2004)), the only unknown variable in Eq. 5 was the reaction time t. Since under these conditions the chemical system deviates from pseudo first-order conditions, the mean concentration of NO inside the reactor was used to analyze the experimental results. The averages of several experiments conducted at different flow rates are shown in Fig. 4a. Method 3 assumes perfect instant mixing and plug flow in the reactor: the calculation for a range of flow rates is shown in Fig. 4b.

All three methods offer internally consistent results, within the respective uncertainties (Fig. 4b). Method 3 agrees well with the acetone injection "means" calculation, but overestimates the residence times determined with method 2 by $\sim$18%. Method 2 relies on well known kinetic parameters and implicitly takes into account the real distribution of flow paths through the reactor. Method 2 also provides a simple test of the TORS functionality using NO instead of a BVOC. 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.

4.2 Ozone wall loss

One of the most important parameters and key uncertainties of the TORS technique is the ozone wall loss (R_{wall}), as discussed in Sect. 2.2. Other species can be lost on the reactor surface, but these are likely to have little or no impact on the determination of the ozone reactivity either because they do not react with O_3 (e.g., multifunctional products of VOC oxidation) or because they are present at very low concentrations.

Measured R_{O3} is obtained by subtracting the loss of $\mathrm{O_3}$ on the reactor wall (R_{wall}) and, if present, to NO (R_{NO}) from the total loss rate of $\mathrm{O_3}$ (Eq. 6). Small changes in the $\mathrm{O_3}$ wall loss could lead to significant variation in the final determination of ozone reactivity. It is therefore important to minimize this parameter in order to reduce the uncertainty of the measurement. In the design stage, several materials and sizes were tested under dry and humid conditions: 1) a glass cylinder (5 x 70 cm), 2) a quartz cylinder (9 x 100 cm), 3) a PFA coil (1.9 x 1524 cm), 4) a PTFE cylinder (9 x 100 cm). Based on these experiments, the large diameter (OD=9 cm, ID = 8.73 cm) PTFE cylinder showed the lowest ozone wall loss and minimal dependence on humidity.

The ozone wall loss was regularly determined during measurements by switching to a flow of zero air instead of the regular sample with a 3-way teflon valve (Fig. 2): in this operating mode there are no reactants (NO or VOCs) in the reactor and the measured ozone reactivity is equal to R_{wall}. During each experiment and measurement period, multiple determinations of the ozone wall loss were made. Figure 5 shows the average R_{wall} determined during a series of laboratory experiments (Sect. 5.1 and Sect. 5.2), as a function of measured humidity, temperature and time. R_{wall} showed a weak dependence on the relative humidity inside the reactor ($R_{\mathrm{wall}} = 9.6 \times 10^{-7} \times \mathrm{RH} + 4.4 \times 10^{-5}$, with R^2 = 0.198). Ambient humidity is usually higher than the range shown in Fig. 5, but because of the dilution of the sample flow by the dry ozone flow before entering the reactor (Fig. 2), the relative humidity in the reactor is always less than 50%. There was no clear dependence of R_{wall} on temperature, at least in the limited range experienced in the laboratory (14-24 $^\circ\mathrm{C}$). The ozone wall loss can be expected to vary with time, as the surface of the reactor is passivated and exposed to ambient air, but there was no obvious temporal trend over the nine month period of these experiments (Fig. 5).

Although there was no clear pattern with respect to the measured parameters, it is apparent that there was significant variability in the ozone wall loss and, therefore, it is necessary to measure R_{wall} often during an experiment and/or ambient measurements. The average standard deviation of R_{wall} was 2.4×10^{-5} $\mathrm{s^{-1}}$ and the interquartile range was $0.5 - 1.2 \times 10^{-4}$ $\mathrm{s^{-1}}$ (mean = 9.8×10^{-5} $\mathrm{s^{-1}}$, median = 7.1×10^{-5} $\mathrm{s^{-1}}$), which corresponds to the reactivity of 21-51 ppb of α-pinene (mean = 41.5 ppb, median = 30 ppb). The range of the measured ozone wall losses suggests that the limit of detection of TORS is of the order of a few tens of ppb of α-pinene or the equivalent concentration, in terms of reactivity, of other BVOCs (Table 1); the limit of detection was quantified with laboratory experiments using known concentrations of α-pinene, as described in Sect. 5.1.

4.3 TORS operation

The flows in the TORS instrument are constrained by several competing factors (Fig. 2): first, the total flow (sample + ozone) must be larger than the inlet flows of both $\mathrm{O_3}$ monitors, which are fixed at $\sim$1.4 slpm each. Second, the residence time in the reactor must be long enough to allow the ozonolysis reactions to take place to a measurable extent, but short enough that the consumption of the reactants does not become significant, so that pseudo first-order conditions are maintained (Sect. 2.2).

During the design phase of the TORS instrument several combinations of flow settings were experimented with, eventually settling on a sample flow of $\sim$2.3 slpm and an ozone flow – composed of a flow of zero air through the ozone lamp, plus a dilution flow to control the concentration of ozone, and a flow of cyclohexane as OH scrubber – of $\sim$1.5 slpm (Fig. 2). These settings result in a reactor flow rate of 2470 sccm, corresponding to a residence time of 140 seconds (Sect. 4.1). Since the sample flow is mixed with the ozone flow (Fig. 2), a correction factor needs to be applied to account for the dilution of the sample by the ozone flow. In the experiments and measurements described in Sect. 5, the mixing ratio of ozone at the entrance of the reactor was $\sim$120 ppb. The instrument settings, such as the residence time and the ozone concentration, can in principle be varied to adjust the sensitivity of TORS for environments with different values of R_{O3}.

Once the flows are set, the basic operation cycle of the TORS instrument consists of 3 main steps:

1. "bypass mode" to check the agreement between the two $\mathrm{O_3}$ monitors: the sample flow is substituted with an equal flow of zero air and the reactor is bypassed for a period of approximately 15 minutes. In this mode, both monitors measure the $\mathrm{O_3}$ concentration in zero air (i.e., with no reactants) before the entrance of the reactor, so that a correction factor can be derived if they differ. In this work, the difference between the $\mathrm{O_3}$ monitors was checked every day at the start and at the end of each experiment/measurement period, and was typically $\sim$1 ppb.

2. "wall loss mode" to determine R_{wall} (Eq. 6): the sample flow is substituted with an equal flow of zero air inside the reactor for a period of approximately half an hour. The effect of the humidity change in the reactor within such a short period of time was found to be negligible. In this work, the wall loss was determined every 2-3 hours.

3. "sampling mode", the main operation mode of the instrument with the sample flow containing BVOCs and/or NO.

This procedure was followed during all the experiments and measurements described in Sect. 5.

5 Evaluation of TORS

The TORS instrument was tested in a series of experiments to evaluate its functionality and potential. The experiments were designed and conducted in order of increasing complexity from individual species in laboratory conditions to the complex BVOCs mixture of a horticultural glasshouse. The TORS instrument was at first tested in the laboratory using pure α-pinene (Sect. 5.1), followed by emissions from small plants (Sect. 5.2). After these tests showed that the instrument was behaving as expected under controlled conditions, it was deployed in a glasshouse containing various aromatic plants to demonstrate that TORS can measure total ozone reactivity under quasi-ambient conditions (Sect. 5.3).

It must be noted that the rate coefficients of $\mathrm{O_3}$ with BVOCs span several orders of magnitude (Table 1). Therefore, for individual species in isolation, a measured ozone reactivity of (for example) $2.36 \times 10^{-5}\ \mathrm{s^{-1}}$ corresponds equally to 1.9 ppm of camphene, 10 ppb of α-pinene, 75 ppb of isoprene, 80 ppt of β-caryophyllene. This affects the interpretation of R_{O3} measurements by TORS, particularly if the composition of the sample is not known, as would be the case when taking ambient measurements.

5.1 Laboratory experiments

Several laboratory experiments were carried out using known concentrations of a selected biogenic compound. A thermostated diffusion tube and pure α-pinene (98%, from Sigma-Aldrich) in zero air were used to provide a constant source of BVOC. The diffusion rate was controlled by varying the temperature of the diffusion tube and determined by regularly weighing it with a precision balance over a period of several weeks. 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%.

The values of R_{O3} measured during several experiments were compared with the values calculated using the known concentrations of α-pinene in the sample (Eq. 6). 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 + O_3 rate coefficient (41%, Atkinson et al. (2004)) (Fig. 6a). At mixing ratios below 10 ppb of α-pinene, the measured reactivities cannot be statistically distinguished from each other and from zero; in fact, the corresponding reactivity ($2.36 \times 10^{-5}\ \mathrm{s}^{-1}$) is of the same magnitude as the average standard deviation of R_{wall} (Sect. 4.2). Measured R_{O3} corresponding to concentrations of α-pinene $>$14 ppb are linearly correlated (r^2 = 0.993) with a slope of $1.2 \times 10^{-6} \pm 1.0 \times 10^{-7}\ \mathrm{s}^{-1}/\mathrm{ppb}$, corresponding to the sensitivity of the instrument, and an intercept of $6.4 \times 10^{-5} \pm 8.5 \times 10^{-6}\ \mathrm{s}^{-1}$ (Fig. 6a).

Based on these experiments, the TORS detection limit, for a residence time of 140 seconds, can be estimated between 4.5×10^{-5} and $9.0 \times 10^{-5}\ \mathrm{s}^{-1}$, corresponding to ozone reactivities equivalent to 20-40 ppb of α-pinene (Table 1). These values are consistent with the estimates based on the range of measured R_{wall}, as discussed in Sect. 4.2; the actual detection limit for a given set of measurements depends on the magnitude of the ozone wall loss, which can vary significantly (Fig. 5). These values are also comparable to the detection limit of the instrument described by Matsumoto (2014) of $1.4 \times 10^{-4}\ \mathrm{s}^{-1}$, for a residence time of 57 seconds. 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 + O_3 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%.

Some experiments were conducted without adding cyclohexane to the ozone flow (Fig. 2) to verify the effect of the OH scrubber, as discussed in Sect. 2.3. Ozonolysis of BVOCs is known to generate OH radicals with different yields (Rickard et al., 1999; Johnson and Marston, 2008) which may lead to consumption of BVOCs by OH in the reactor, thus causing underestimation of R_{O3}. However, the experiments where the OH scrubber was used did not show substantially different results from those where it was not used (Fig. 6b). Measured R_{O3} with $\sim$ 30 ppb of α-pinene was $6.2 \times 10^{-5} \pm 2.2 \times 10^{-5}$ s^{-1} with cyclohexane and $5.8 \times 10^{-5} \pm 1.9 \times 10^{-5}\ \mathrm{s}^{-1}$ without cyclohexane: the corresponding p-value was 0.394, indicating that the difference between the two measurements is not statistically significant. The difference between the ozone reactivities determined with and without OH scrubber was 6-7%, in agreement with the modelling results (Sect. 2.3). While this is less than the precision of the ozone monitors (Sect. 3.1) we note that, in principle, the comparison of total ozone reactivity measurements with and without an OH scrubber can yield additional information on the speciation of the VOC mixture in the sample.

5.2 Plant experiments

Laboratory experiments were carried out using small aromatic plants in a controlled environment to test the TORS instrument under more realistic conditions. Three plants of lemonthyme (*Thymus citriodorus*) were enclosed in a Teflon bag (Adtech Polymer Engineering Ltd, UK) with an approximate volume of 0.1 m^3, filled with a continuous flow of zero air. A halogen lamp

(ROK 120W) was located over the bag and a temperature/humidity probe (Vaisala HMP110) was inserted into the bag, together with a small fan (RS Components) to ensure homogeneous conditions. The natural release of water vapour via transpiration and evaporation by the plants caused the humidity in the bag to rise over the course of the experiment, but relative humidity remained below 50% inside the TORS reactor due to dilution with the dry ozone flow (Fig. 2) and therefore it did not affect the loss of O_3 on the reactor wall, as discussed in Sect. 4.2. The PTR-MS was connected to the bag to identify and quantify the BVOCs that constitute the plant emissions (Sect. 3.2). The TORS instrument and the PTR-MS sampled continuously from the Teflon bag during the experiment, which had a duration of about 48 hours.

Figure 7 shows the ozone reactivity measurements of one lemonthyme experiment, together with the reactivity calculated using the BVOCs measurements by PTR-MS. The interquartile range of measured R_{O3} was $3-10\times10^{-5}$ s^{-1} for the first experiment and $6-9\times10^{-5}$ s^{-1} for the second experiment, with mean values of 6.5×10^{-5} and 8.1×10^{-5} s^{-1}, respectively. Measured ozone reactivity increased by about a factor of 2 when the lamp was turned on, due to increased emissions of all BVOCs and, in particular, of the more reactive ones (i.e., monoterpenes and sesquiterpenes, Table 1). This is because when the lamp was switched on, the temperature inside the bag increased (by ∼10 °C, Fig. 7), as well as the light. Isoprene emissions are controlled by both light and temperature, but monoterpenes and sesquiterpenes emissions are mostly controlled by temperature and have an exponential response to temperature (Duhl et al., 2008; Guenther et al., 2012; Hellén et al., 2018). Therefore, the emissions of these more reactive compounds tend to increase faster than those of isoprene when temperature rises quickly.

To calculate R_{O3} from the PTR-MS measurements using Eq. 6, a number of assumptions have to be made. The only BVOC that the Proton Transfer Reaction technique can uniquely identify is isoprene. All monoterpenes and sesquiterpenes have the same molecular weight (136.24 and 204.36 g/mol, respectively) and therefore are very difficult to distinguish from each other using a soft ionization technique (de Gouw and Warneke, 2007). Thus, the PTR-MS instrument effectively reports the sum of monoterpenes and the sum of sesquiterpenes. To account for this problem, estimated low and high R_{O3} limits were calculated. Lemonthyme is an evergreen broadleaf plant, whose main emissions (besides isoprene) are α-pinene, β-pinene, β-ocimene (monoterpenes) and β-caryophyllene, α-farnesene (sesquiterpenes) (Fares et al., 2011; Guenther et al., 2012). The lower limit R_{O3} estimate was calculated assuming that the measured monoterpene signal was solely due to β-pinene and that the measured sesquiterpene signal was solely due to α-farnesene. The higher limit R_{O3} estimate was calculated assuming that the measured monoterpene signal was solely due to β-ocimene and that the measured sesquiterpene signal was solely due to β-caryophyllene. This provides a range of R_{O3} which likely includes that of the particular BVOCs mixture emitted by the lemonthyme plants (Table 1). The calculated low and high R_{O3} limit estimates are compared to the TORS measurements in Fig. 7. The TORS measured reactivities were within the range of these estimates and followed the same pattern, with higher values when the light was on and the temperature higher.

5.3 Glasshouse experiments

In order to evaluate the TORS technique under quasi-ambient conditions, the instrument was deployed in a horticultural glasshouse containing a range of aromatic plants. The glasshouse is a similar environment to ambient and was subject to a continuous inflow of ambient air, but, being a semi-enclosed system, the concentrations of BVOCs emitted from the plants are higher and the concentrations of NO lower than the external environment, resulting in a stronger R_{O3} signal. The glasshouse is located at the Winterbourne House and Garden (https://www.winterbourne.org.uk/), adjacent to the University of Birmingham campus, and has an approximate volume of 200 m^3. The following plants were inside the glasshouse during the sampling period: Fringed "French" Lavender (*Lavandula dentata var. candicans*), Lemon Verbena (*Aloysia triphylla*), Scented Leaf Geraniums (*Pelargonium x citriodorum* "Prince of Orange", *Pelargonium Radula*) and several varieties of the Citrus genus (*Citrus x limon*, *Citrus x latifolia* "Tahiti", *Citrus reticulata* "Clementine").

The TORS instrument was set up in a similar way as in the plant experiments (Sect. 5.2), with regular determinations of the ozone wall loss using a flow of zero air instead of the ambient flow. The ozone wall loss during the measurement period varied between 4.9×10^{-5} and 1.1×10^{-4} s^{-1} (first and third quartiles), with mean values between 0.7×10^{-4} and 1.1×10^{-4} s^{-1}. The measurements were taken over a period of two weeks in early June 2018; during this period the weather was dry (mean RH = 57%) with temperatures reaching a maximum of 39 °C inside the glasshouse (mean = 15 °C). Cyclohexane was used as OH scrubber only during the second week of measurements. The PTR-MS was not available at the glasshouse, but two air samples were taken on two different days using adsorption tubes and qualitatively analyzed by GC-MS (Sect. 3.2). The GC data were used to determine the most important monoterpenes and sesquiterpenes in the air inside the glasshouse, based on their relative abundance.

The total ozone reactivity measurements made in the glasshouse are shown in Fig. 8. For the period without cyclohexane the interquartile range was $1.9 - 4.6 \times 10^{-4}$ s^{-1} with a mean value of 3.3×10^{-4} s^{-1}. For the period with cyclohexane the interquartile range was $2.0 - 4.2 \times 10^{-4}$ s^{-1} with a mean value of 3.3×10^{-4} s^{-1}. Taking into account the natural variability of plant emissions, these numbers suggest that the use of an OH scrubber does not change significantly the TORS measurements, in keeping with the laboratory experiments (Sect. 5.1) and the model results of the chemistry inside the reactor (Sect. 2.3).

In the absence of BVOC measurements, an estimate of the ozone reactivity was calculated using the qualitative information obtained from the GC-MS analysis of the adsorption tubes and from the emission factors by Guenther et al. (2012): broadleaf evergreen plants emit isoprene, monoterpenes and sesquiterpenes in a proportion of approximately 1:0.1:0.02. However, Fares et al. (2011) found that Citrus plants, several types of which were present on the glasshouse, emit more monoterpenes than isoprene. Since most monoterpenes are more reactive with ozone than isoprene (Table 1), the estimates of R_{O3} discussed below are relatively insensitive to the actual isoprene concentration. Analysis of the adsorption tubes showed that the most important monoterpenes were limonene, β-pinene, camphene, myrcene, and the most important sesquiterpenes were longifolene and farnesene. Based on these results, a high R_{O3} was estimated assuming 100 ppb of isoprene, 25 ppb of myrcene and 5 ppb of α-farnesene. A low R_{O3} was estimated assuming 50 ppb of isoprene, 5 ppb of camphene and 1 ppb of longifolene. The estimated low and high R_{O3} were of the same magnitude as the TORS measurements (Fig. 8).

In contrast to the laboratory experiments, which were performed using zero air (Sect. 5.1 and Sect. 5.2), the ozone reactivity measurements in the glasshouse were affected by ambient NO (R5). Measurements of NO were not available inside the glasshouse, so it is not possible to definitively quantify the contribution of R_{NO} to the total ozone reactivity measurements shown in Fig. 8. The average total ozone reactivity showed a clear diel pattern, with maximum values of about 5.2×10^{-4} s^{-1} observed around 06:00 (approximately one hour after dawn), and was anticorrelated with ambient temperature (Fig. 8).

BVOCs emissions are driven by both light and temperature and are therefore higher during the day (Fares et al., 2011; Hellén et al., 2018); likewise, NO concentrations are higher during day, due to traffic emissions. Therefore, it may be expected that measured total ozone reactivity (from both BVOCs and NO) is higher during the daylight hours, which was in fact observed during the laboratory experiments with the lemonthyme plants (Fig. 7). However, under ambient conditions, BVOCs react during the day with OH radicals at a faster rate than they react with $\mathrm{O_3}$ (Atkinson et al., 2006; Johnson and Marston, 2008): as a result, ozone reactivity tends to peak in the early morning, when the NO and BVOCs emissions start increasing, but the concentration of OH is still too low to compete with $\mathrm{O_3}$ for BVOC removal (Hellén et al., 2018).

6 Summary and Future Work

An instrument to measure total ozone reactivity, the Total Ozone Reactivity System (TORS), was developed, characterized and tested under controlled conditions in the laboratory; both individual compounds and small plants were used. The instrument was deployed inside a horticultural glasshouse containing a range of aromatic plants to evaluate its functionality under quasi-ambient conditions.

The TORS instrument was able to measure $\mathrm{O_3}$ reactivities with BVOCs (R_{O3}) of $4.5 - 9.0 \times 10^{-5}\ \mathrm{s^{-1}}$ 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. 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. An OH scrubber (cyclohexane) was used to remove the OH radicals formed by the ozonolysis of BVOCs; however, simulations of the chemistry inside the TORS reactor using a Master Chemical Mechanism (MCM v3.3.1) box-model found that the formation of OH from BVOC + $\mathrm{O_3}$ reactions affected the measurements of R_{O3} by $<$6%, under the conditions used during the experiments.

Further work will aim to improve the stability of the signal, and to reduce the signal noise and the detection limit. This may require using ozone monitors with higher precision and/or a more stable $\mathrm{O_3}$ generator, as well as a detailed exploration of the various parameters affecting the TORS technique: gas flows, residence time, relative humidity, OH scrubber levels, ozone concentrations. Moreover, our experimental data indicate that accurate measurements of $\mathrm{NO_x}$ are always required to be able to interpret the TORS observations. 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, to improve understanding of the role of natural emissions on the ozone budget and the oxidative capacity of the atmosphere.

Data availability. The original data are available on request from the authors.

Competing interests. The authors declare no competing interests.

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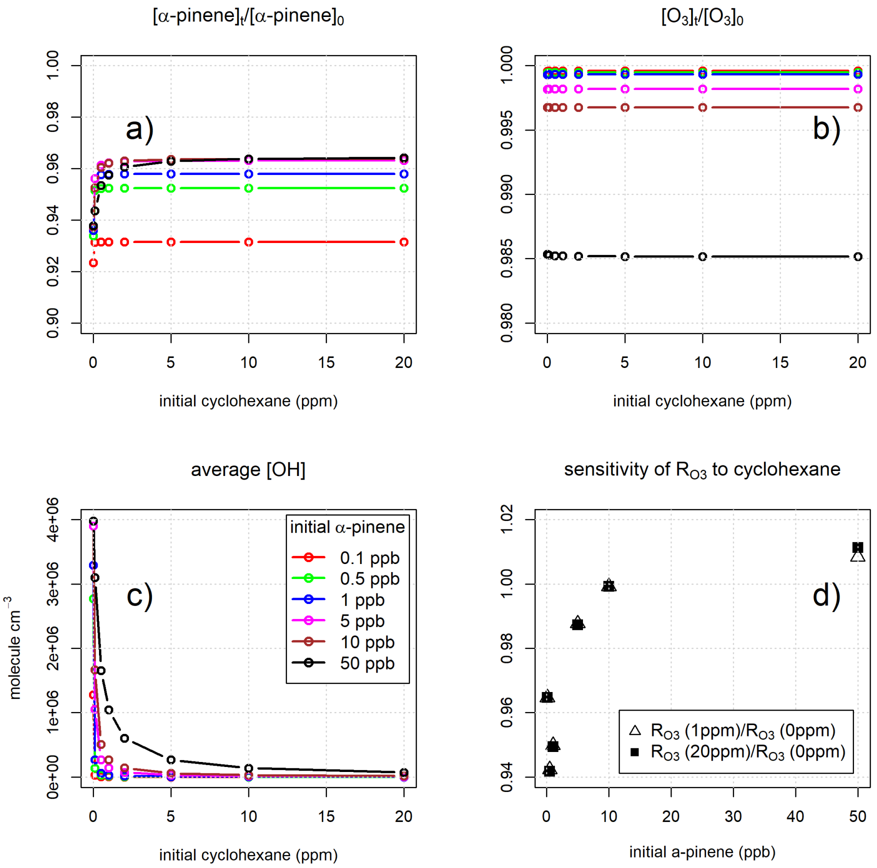

Figure 1. (a-b) Modelled removal of α-pinene and O_3 (relative to their initial concentrations) as a function of cyclohexane level. (c) Average modelled concentrations of OH as a function of cyclohexane level. (d) Sensitivity of modelled R_{O3} to cyclohexane level as a function of α-pinene mixing ratio.

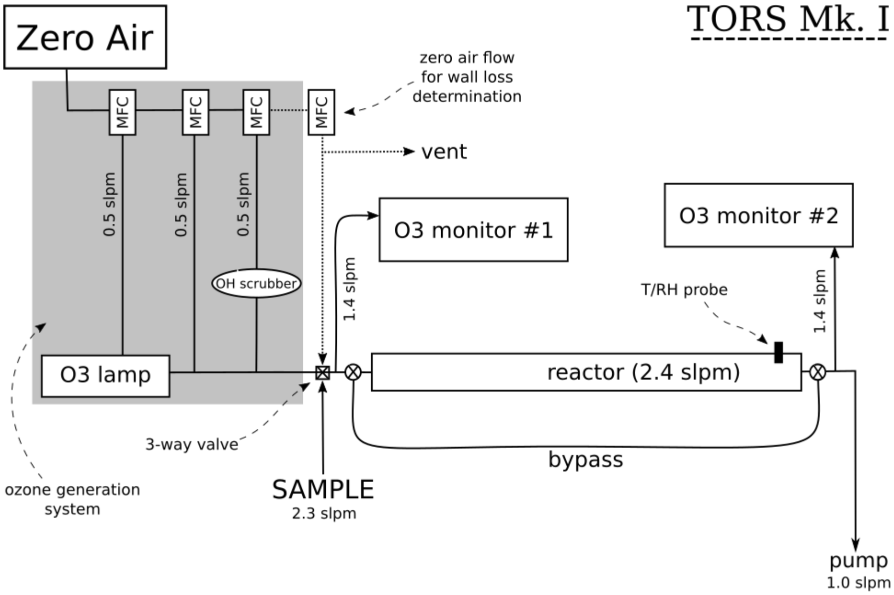

Figure 2. Diagram of the TORS instrument with typical flow settings (Sect. 4.3).

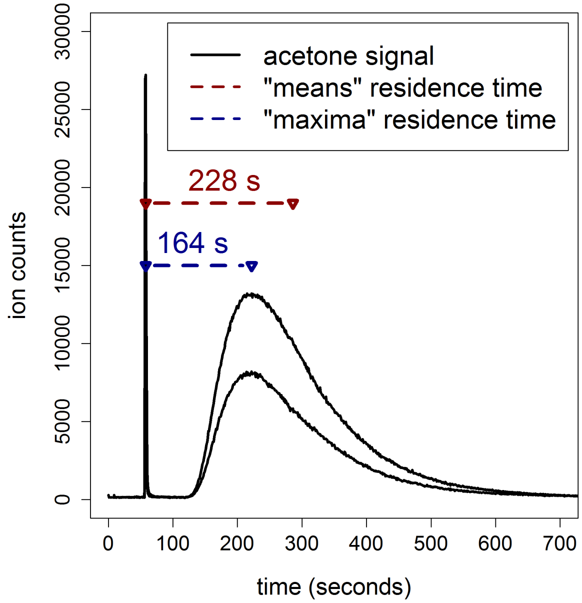

Figure 3. Two acetone double injection experiments used to estimate the residence time in the PTFE reactor for a flow rate of 1600 sccm. The "maxima" calculation uses the differences in time of the peak acetone signals; the "means" method uses the differences between the mean elapsed time of the two acetone signals.

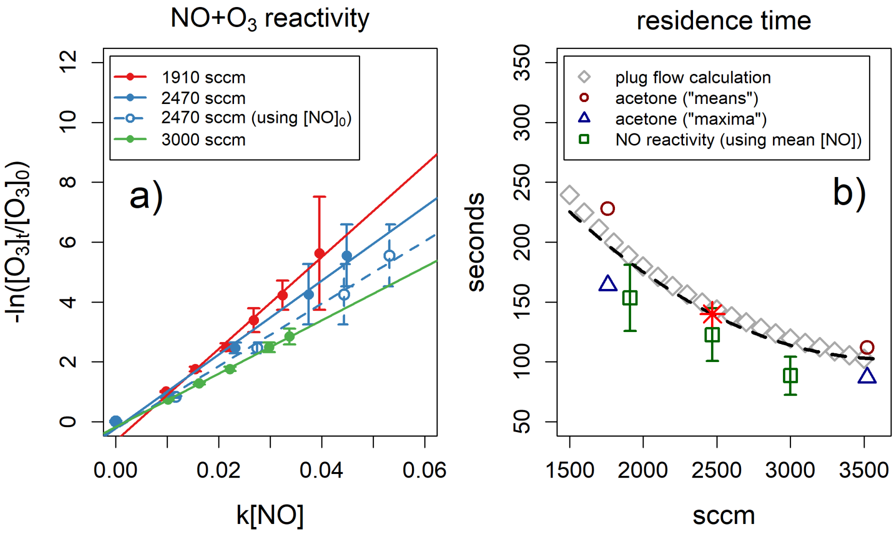

Figure 4. (a) NO reactivity experiments analyzed using the mean NO concentration inside the reactor. One experiment analyzed using the initial NO concentration is also shown, for reference. (b) Residence times as a function of reactor flow – determined by three different methods – and polynomial fit 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).

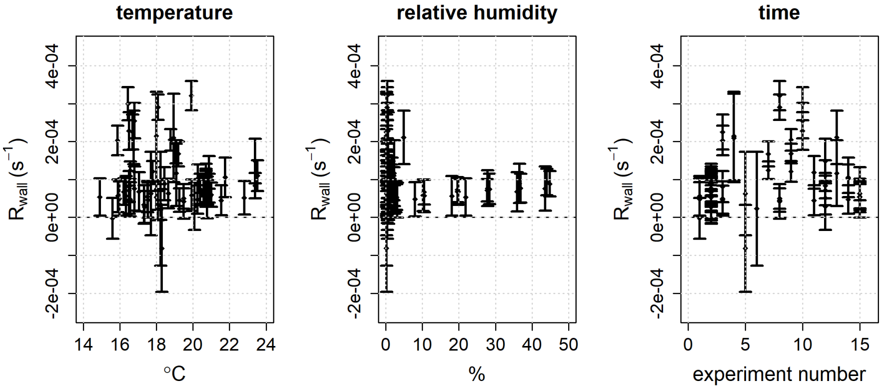

Figure 5. Mean and 2σ standard deviation of the ozone wall loss (R_{wall}) in the PTFE reactor as a function of humidity, temperature and time. The data are taken from 15 experiments, with multiple determinations of R_{wall} per experiment, over a nine month period.

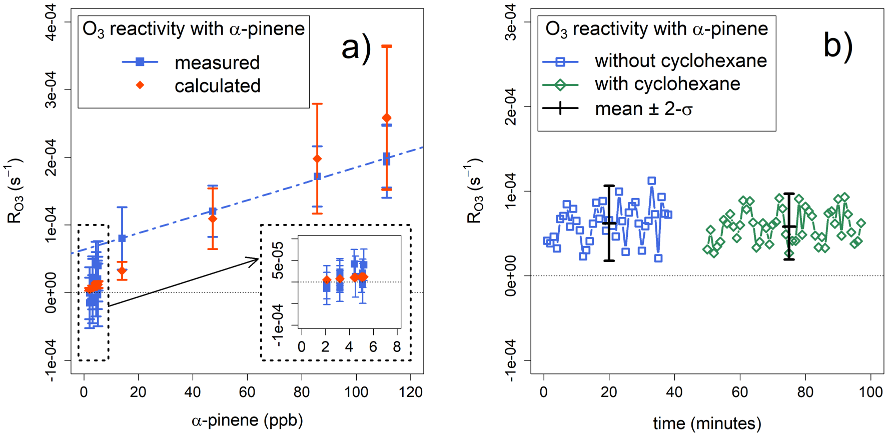

Figure 6. (a) Measured and calculated mean ozone reactivities with α-pinene. The blue dashed line indicates the linear regression of the measured R_{O3} values for α-pinene mixing ratios >20 ppb. (b) Ozone reactivity with α-pinene measured with and without cyclohexane as OH scrubber.

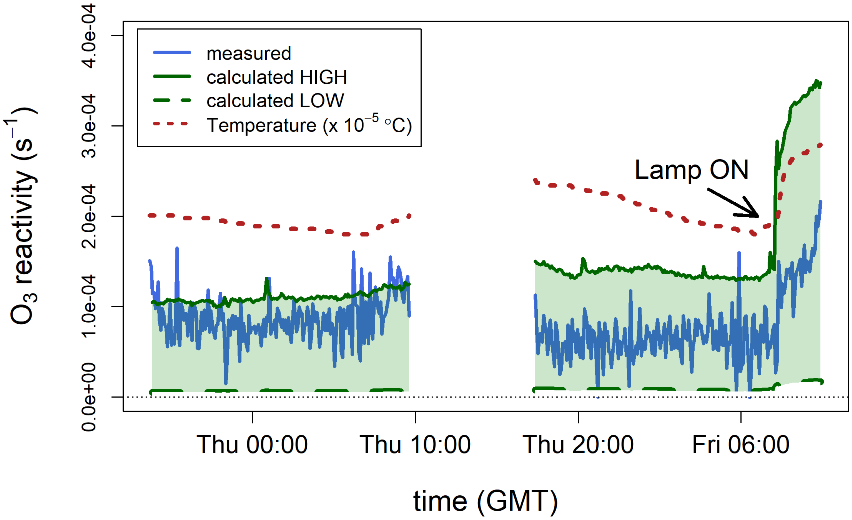

Figure 7. Measured ozone reactivity (R_{O3}) from 3 plants of lemonthyme (*Thymus citriodorus*) in a Teflon bag, compared to the ozone reactivity calculated from BVOCs measurements by PTR-MS. The temperature (in °C) measured inside the bag is also shown. All data are averaged to 5 minutes.

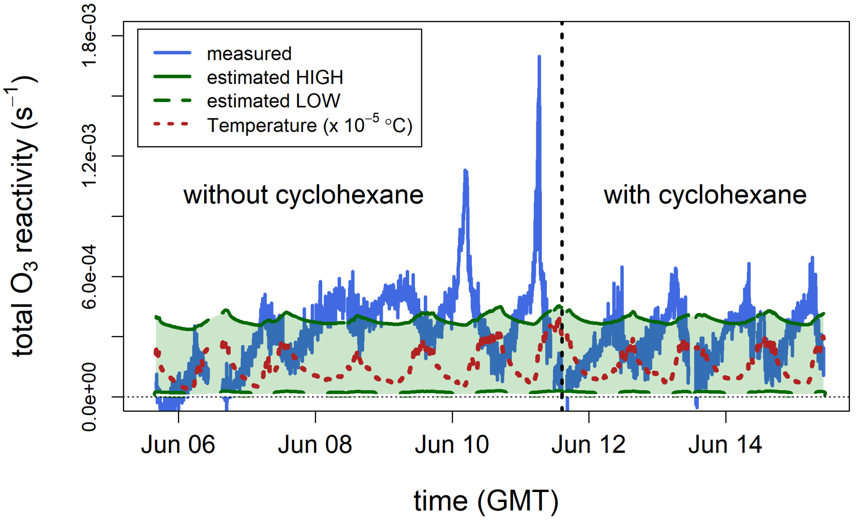

Figure 8. Total ozone reactivity (R_{O3} + R_{NO}) measured in the Winterbourne House and Garden glasshouse compared to the ozone reactivity calculated from estimated concentrations of BVOCs. The temperature (in °C) measured inside the glasshouse is also shown. All data are averaged to 5 minutes.

Table 1. Rate coefficients of the reactions with ozone (k_{O3}, in $\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$), chemical lifetimes for $[O_3]$ = 120 ppb (τ, in min), absolute ozone reactivities (R_{O3}, in $\mathrm{s^{-1}}$), and relative ozone reactivities (with respect to α-pinene) of selected BVOCs and inorganic compounds. The rate coefficients are from Atkinson et al. (2004, 2006) and calculated for standard conditions (298 K, 1 atm); the ozone reactivities are calculated for mixing ratios of 1 ppb of each species.

Class	Species	k_{O3} ($\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$)	τ (min)	R_{O3} ($\mathrm{s^{-1}}$)	relative R_{O3}
hemiterpenes	isoprene	1.28×10^{-17}	441.4	3.15×10^{-7}	0.13
monoterpenes	α-terpinene	1.90×10^{-14}	0.3	4.68×10^{-4}	197.97
	β-ocimene	5.10×10^{-16}	11.1	1.25×10^{-5}	5.31
	myrcene	4.70×10^{-16}	12.0	1.16×10^{-5}	4.90
	limonene	2.20×10^{-16}	25.7	5.41×10^{-6}	2.29
	α-pinene	9.60×10^{-17}	58.8	2.36×10^{-6}	1
	sabinene	8.30×10^{-17}	67.9	2.04×10^{-6}	0.86
	3-carene	4.90×10^{-17}	115.1	1.21×10^{-6}	0.51
	β-pinene	1.89×10^{-17}	297.6	4.67×10^{-7}	0.20
	camphene	5.02×10^{-19}	11229.3	1.24×10^{-8}	0.01
sesquiterpenes	β-caryophyllene	1.20×10^{-14}	0.5	2.96×10^{-4}	125.03
	α-farnesene	5.88×10^{-16}	9.6	1.45×10^{-5}	6.13
	α-copaene	1.50×10^{-16}	37.6	3.69×10^{-6}	1.56
	longifolene	5.00×10^{-19}	11279.6	1.23×10^{-8}	0.01
inorganic	NO	1.89×10^{-14}	0.3	4.65×10^{-4}	196.56
	HO_2	2.01×10^{-15}	2.8	4.96×10^{-5}	20.99
	NO_2	3.52×10^{-17}	160.3	8.67×10^{-7}	0.37