

## ***Interactive comment on “An instrument for in-situ measurement of total ozone reactivity” by Roberto Sommariva et al.***

### **Anonymous Referee #2**

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#### **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

C1

want to express during the demonstration of the instrumental test.

#### **B. Important specific comments:**

B1) Line 101 and followings: Quantitative descriptions on contribution of NO<sub>2</sub> should be corrected. The reviewer thinks that 1 ppbv of NO<sub>2</sub> corresponds to  $3.52/9.6 = 1/2.7 = 0.37$  ppbv of  $\alpha$ -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 NO<sub>2</sub> should be checked again, including descriptions in Sect. 5. Please do not mislead readers.

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.

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.

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.

B5) Fig.4 & Sect.4.1 (especially, on NO+O<sub>3</sub> reaction): In 'Method 2 (Fig.4a)',  $k[\text{NO}]$  up to 0.05 (maybe in the unit 's<sup>-1</sup>'? 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 O<sub>3</sub> are similar. The reaction NO+O<sub>3</sub> is fast. Then, both NO and O<sub>3</sub> can significantly decrease within the reaction time. (Question:) Are the settings of the experiments, calculations, and discussion to determine the reaction

C2

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 O<sub>3</sub> and NO, for example, till t = 150 sec, NO decreased from 100 ppbv to 5 ppbv and O<sub>3</sub> decreased from 120 ppbv to 25 ppbv. NO can drastically decrease during the reaction time due to its fast reaction with O<sub>3</sub>. [Q2] In Fig.4a, we can estimate the reaction time. For example, in case of 2470 sccm, for k[NO] = 0.04 (s<sup>-1</sup>?), -LN(O<sub>3</sub>(t)/O<sub>3</sub>(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? Additionally, as an associated question, what value of k(NO+O<sub>3</sub>) was applied in this study? Authors indicate the values as '1.89x10<sup>-14</sup>' in Table 1 and '1.73x10<sup>-14</sup>' 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.

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?

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

C3

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 RO<sub>3</sub> was captured during the experiment. (Assumption & Caution) Authors want to discuss on BVOCs contribution to captured RO<sub>3</sub> 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 RO<sub>3</sub>. 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 RO<sub>3</sub> (Fig.9). Then BVOCs contribution to RO<sub>3</sub> was indicated as ?? in Fig.9. . . . Other associated comments are shown as follows: 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 RO<sub>3</sub>) should be indicated, because they are essential for us to discuss NO contribution to RO<sub>3</sub> in Fig.9. For example, does NO really show the daytime peak as Fig.9? Does NO indicate its variation similar to RO<sub>3</sub>? 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.

C4

B8) Sect. 5.3, about O<sub>3</sub> and NO<sub>2</sub> in the glasshouse: Authors consider that NO concentration in the house is smaller than ambient. Then, how about O<sub>3</sub> and NO<sub>2</sub> concentrations in the house? Is the glasshouse enclosed by walls? Or, can ambient air pass through the house? As a result, how much are O<sub>3</sub> and NO<sub>2</sub> concentrations in the house, do you think? Are O<sub>3</sub> and NO<sub>2</sub> in the house significant for RO<sub>3</sub> measurement?

B9) Fig.9, about the diurnal variation of BVOCs contribution to RO<sub>3</sub>: 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 RO<sub>3</sub> has daytime peak. Would you please add explanations and your opinions on such diurnal variation of BVOCs contribution?

B10) Around Line 455, about the lifetime of NO by O<sub>3</sub> reaction:  $k$  is about  $2 \times 10^{-14}$ , [O<sub>3</sub>] (30 ppb) is about  $7.5 \times 10^{11}$ , then  $k[\text{O}_3]$  is about  $1.5 \times 10^{-2} \text{ s}^{-1}$ . Thus, the lifetime of NO is about 67 sec ( $= 1/(1.5 \times 10^{-2} \text{ s}^{-1})$ ). This error is critical for the authors' consideration that NO can be reduced to 20 % of ambient level due to O<sub>3</sub> reaction in the sample tube (4 sec). Associated to the comment B8, can ambient NO react with residual O<sub>3</sub> in the glasshouse before the sampling inlet? Please consider them again and reconstruct the descriptions.

C. Other comments and Technical corrections:

C1) Line 29: 'state' → 'states' ?

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.

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  $\alpha$ -pinene and cyclohexane? but the scavenger is not BVOC . . . )

C5

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

C5) Line 91 'R11' → 'R2', too?

C6) Line 131 'R5-R8' → 'R6-R8'?

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

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

C9) Lines 178-184 and Fig.1d: In Fig.1d, RO<sub>3</sub>(with)/RO<sub>3</sub>(w/o) (please add the axis name in the figure) are  $\sim 0.965$  at  $\alpha$ -pinene = 0.1 ppb and  $\sim 0.950$  at 0.5 ppb. That is, RO<sub>3</sub>(w)/RO<sub>3</sub>(wo) ratio decreases while  $\alpha$ -pinene < 0.5 ppb, and then increase for  $\alpha$ -pinene > 0.5 ppb. Would you please add brief explanations on this trend?

C10) Line 193 'ambient measurements' → Strictly, 'ambient, not always, but nighttime & high NO<sub>x</sub> & low NO' ? Please clarify the 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'.

C12) Line 267 'Eq.3' is not correct. the reviewer recommends that this manuscript be acceptable after minor revisions.

C13) Around Line 294: Please clarify, anywhere in the sentences earlier, what the 'central? 0.5 slpm flow of zero air (without O<sub>3</sub> 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.)

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

C6

C15) Scientific names of plants: Italics?

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

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

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

End of Comments.

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