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Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #1

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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.

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

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

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

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

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.

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

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).

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

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

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.

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).

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

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

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?

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

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?

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?

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?

Page 10, line 292: Please quantify the 'small but noticeable dependence of Rwall on humidity'.

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

Page 11, line 298 onwards: What is the standard deviation and median of the mea-

sured ozone wall loss? Can the limit of detection be quantified more precisely using the observed variability in the ozone wall loss?

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?

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

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

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

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.

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

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?

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

Page 14, line 408: Please provide some approximate quantification for the statement 'concentrations of BVOCs ... are higher and the concentrations of NO lower ...'.

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

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

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

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

Page 15, line 458: What is the basis for the assumption of NO in the reactor being ∼20 % of the ambient concentration?

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.

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