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Interactive comment on “The Comparative Reactivity Method – a new tool to measure total OH reactivity in ambient air” by V. Sinha et al.

V. Sinha et al.

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We thank the anonymous reviewers for their helpful comments and encouraging remarks about the high impact of the work and how this work has the potential to rapidly improve our understanding of VOCs and oxidation processes in the atmosphere. Before addressing the minor specific comments of the reviewers, we would like to clarify that the CRM method would work quite well even in ambient air environments with up to 10ppb NO. One of the remarks of Reviewer 1 is that at $\text{NO} < 5$ ppb, measurements from the instrument are valid. It was perhaps not so clear from our wording in the discussion paper that the 5 ppb value corresponds to the NO mixing ratio within our set up, which is after dilution of the sampled air within the set up. As the sampled ambient air is diluted by a factor of 1.7- 2 (see also Line 1 , Page 18201 of the discussion paper) within the set up, it is possible to measure OH reactivity accurately with

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the existing configuration even in ambient air environments containing up to 10 ppb NO (5 ppbv times the dilution factor). We have made this more clear in the revised version and specify whether we are referring to NO in the setup or NO in the ambient air, throughout the text in the revised version.

Detailed below are replies to specific comments of the reviewers.

Reviewer 1

Comment :

Abstract. A very important aspect of the paper is the determination of possible interferences which could complicate the determination of the reactivity measurement and lead to errors. Three of these are investigated later in the paper, (a) Photoysis of pyrrole, (b) recycling of HO₂ to OH, and (c) differences in humidity between sampled air and the zero air used to make the OH. These should at least be listed in the abstract, and a typical range of conditions where it works listed.

Reply:

Abstract : In the revised version we have modified the abstract to include the uncertainty of the method and a discussion of the interferences and their potential impact on the method. The following new lines have been added to the abstract in the revised version:

The present dynamic range for ambient air reactivity is about 6 to 300 s⁻¹, with an overall uncertainty of 25% above 8 s⁻¹ and up to 50 % between 6 - 8 s⁻¹. Potential interferences such as high NO in ambient air, varying relative humidity and photolysis of pyrrole within the setup have also been investigated. While interferences due to changing humidity and photolysis of pyrrole are readily overcome by ensuring that humidity in the set up does not change drastically and the photolytic loss of pyrrole is measured and taken into account, NO > 10 ppb in ambient air remains a significant interference for the current configuration of the instrument.

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Comment: Page 4. Equation (2), need a square bracket around OH as it is a change in concentration with time.

Reply: Done

Comment: Page 6, 3 lines below equation (3), again [OH] Equation (4), [OH]

Reply : Done

Comment: Page 7, units of OH concentration are molecule cm⁻³,

Reply: Done

Comment: Page 8. End of paragraph 2, worth adding a sentence that the fate of the H atoms will be discussed later in the paper (I was left wondering about this).

Reply: We have modified Line 21, Page 18187 of the discussion paper to include mention of the H radicals now: " When the lamp is switched on, OH and H radicals are produced due to photolysis of the water vapour (at the 184.9 nm wavelength) "

Comment: Page 9, space after the reference after ... Werneke, 2007).

Reply: Done

Comment: Page 12, "The method is limited for reactivities < 6 s⁻¹. A comparison should be made here with other methods8230;.. It is interesting to note that limitation is controlled by change in pyrrole concentration that can be made using the PTR-MS when the concentration is very low to begin with"

Reply: We have added the following line in the discussion section (Line-4, Page 18201) where the LIF and CRM technique inter comparison is mentioned. It is worth mentioning here that the LIF based methods can measure OH reactivity in the sub 6 s⁻¹ range, provided NO is not too high. For the case described in Lines 19-24, Page 18192 of the discussion paper, the limitation is indeed controlled by change in pyrrole concentration that can be measured using the PTR-MS. However a concentration of 1 $\mu\text{mol} / \text{mol}$ is

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not low for a PTR-MS, considering that the noise at such levels is high (e.g. precision error is higher than 6%).

Comment: Page 13. 3 Lines from bottom. Does the slope of 0.79 after the correction then imply that the agreement with the expected reactivity (from the calibration) is worse than before the correction? But the point made is that the difference from 1.00 is within the uncertainties?

Reply: Yes, indeed the point made is that the difference from 1.00 is within the uncertainties.

Comment: Page 15, reaction (R11), the rate coefficient above the arrow needs units

Reply: Done

Comment: In common with other methods, HO₂ recycling to OH is a problem when NO is elevated. At the end of P15 it states that the measured OH reactivity tends to zero at 10 ppb NO. Does this mean then that for polluted urban areas where NO can easily reach this value, that it is not possible to make reactivity measurements, as a correction cannot be made to such a reactivity? The simulations for 10 ppb show a correction from 16.5 s⁻¹ to 5 s⁻¹, which is quite a big change. I am pleased though to see that the issue of recycling to OH has been addressed properly via detailed modelling in this paper about OH reactivity measurements. Clearly measurements in urban areas where reactivities are high but also NO is high are going to be difficult. It would be worth a brief discussion of where (i.e. at which concentrations of NO) the other methods fall down. Measurements for example have been reported for New York city and also Tokyo where NO must be very high.

Reply: As mentioned at the outset of this response, up to 10 ppb NO in ambient air would not be a problem for the method. Again, results for the simulation of 10 ppb NO in the setup should be viewed keeping in mind that this would correspond to a rather high value of 20 ppb NO in ambient air, considering the dilution factor of 1.7-2 in the

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set up for ambient air. Further studies to detail the NO interference in the set up will be presented in the near future. As we could not find studies based on the LIF method that detail the NO values and reactivity ranges at which the LIF methods " falls down ", we are unable to comment and make comparisons with the NO interference for the LIF methods .

Comment: The humidity complication would not appear to be a major one as long as the zero air is humidified to a similar extent to that of the ambient air.

Reply: This is correct

Comment: Page 18. The uncertainties for different reactivities given in the discussion on p18 should be stated in the abstract.

Reply: Done

Comment: Page 19. Ozone is generated at the ppm level, and this can react with pyrrole, but is shown to be a minor loss of pyrrole. Does the ppm level of ozone reacting with either OH or HO₂ have to be taken into consideration? Also, for 1×10^{12} levels of radicals, does one need to consider any OH+HO₂ reaction?

Reply: This is not necessary as the contribution of these HO_x and O₃ reactions to the production or destruction of OH radicals within the setup does not change appreciably in the presence of ambient air due to their low levels of ambient abundance (ppb for O₃ and ppt for HO_x) when compared with the levels already within the set up (ppm for O₃ and ppb for HO_x). It is also worth mentioning that reactions involving the OH radical and ambient HO₂ and O₃ are not important because of the very short lifetime of OH with respect to pyrrole (less than 4 milliseconds), in the set up. We have added this clarification in the revised version (place added: Page 18201 of the discussion paper, L12).

Comment: Page 21. It is perhaps worth differentiating the two LIF methods of Ren et al and Sadanaga et al.

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Reply: We are only focusing on the range of reported OH reactivity values from different city environments, and do not think that a discussion and differentiation of the instrumental techniques used therein, is necessary for our interpretation and conclusions.

Comment: The figures are of fairly good quality. The writing is too small in several instances, e.g. on the legends and on some of the plots. The size of the symbols should also be increased on some of the plots. Figure 10. Say more explicitly which species are included in the calculations of the OH reactivity (which isoprene oxidation products). Clearly, in the future more measurements in such an environment over a diurnal profile will be most revealing.

Reply: We agree wholeheartedly with the reviewer that future measurements from forested environments such as tropical rainforests, would help improve our understanding of photochemical processes and the OH budget. In keeping with the suggestion of the reviewer, Figures 4, 5, 6, 7, 8, 9 and 10 have been modified to enlarge the symbols and legends on the axes and the plots. In Figure 10, we will make it more clear that the isoprene oxidation products considered for the calculation are methyl vinyl ketone (mvk) and methacrolein.

Reviewer 2

Specific Comments:

The uncertainty/error analysis presented (p. 18192, line 3-7) is unclear. Does this analysis include uncertainty in the calibration (ability to produce an accurate and precise amount of OH based on flows, etc)? Do the error bars presented (and the 20-25% uncertainty referred to in the paper) include the uncertainty introduced by the pyrrole/OH ratio correction factor (line 23, p.18193) and/or the systematic uncertainty introduced by relative humidity effects (Figure 9)?

Reply: We have made this clearer in the revised version. As the amount of OH radi-

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cals available for reaction with pyrrole and other sinks (when ambient air is sampled) is given directly by the titration of pyrrole with OH at the start of every measurement session, and these values are measured directly, this does not add significant additional uncertainty to the measurements. As mentioned in p. 18192, line 3-7, the uncertainty due to the precision error of the PTR-MS measurement signal (6%) and slight flow fluctuations (10 %) are included in the error analysis. Applying the root square propagation of uncertainties due to 1) rate coefficient of pyrrole + OH (14%), 2) overall flow fluctuation (10%), 3) uncertainty in value of the pyrrole standard (5%) 4) precision error (6%), we get an overall error of 18.89 % which is rounded off to 20%. As the fit used for deriving the correction factor based on the pyrrole / OH ratio passes through all the points (Fig.6), it does not add " extra " uncertainty. Note also that by itself the method is not dependent on calibrations with propane or other gas standards to be capable of measuring OH reactivity of ambient air. The regular tests with gas mixtures of known reactivity only serve the purpose of showing that the method is able to account for the reactivity of known gas mixtures within the uncertainties, ensuring greater confidence in the results. As a result of slight changes in the humidity during measurements of ambient air over an entire diel cycle, an additional uncertainty can be introduced and this has been included in the ambient air data shown for Mainz (Fig. 10) (Error bars > 20%).

Technical corrections:

Comment: Reference required for the first sentence of the Introduction

Reply: The required reference of Goldstein et al., 2007 has been added.

Comment: P.18182: subscript required for bracket after k

Reply: Done

Comment: Fig. 3: Figure caption should explain what the grey bars mean, and what is meant by " modulation of propane "

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Reply: We have added a mention of what the grey bars mean to the figure caption. The grey bars refer to periods wherein propane was introduced into the setup. We note that the figure caption refers to "modulation of propane" and this simply refers to the increase in the pyrrole signal (modulation) from the baseline value of C2, whenever propane was introduced.

Comment: Figure 4,7. The figure caption should explain what the error bars mean (ie, measurement standard deviation or calculated uncertainty including instrument precision, flow rates, etc.?)

Reply: We have added the note "error bars represent the total calculated uncertainty", to the figure captions.

Comment: Figure 9. The figure caption should explain what the colours mean (ie, what does the 14.08.05 refer to?)

Reply: We have changed the legend on the figure itself, so that it is clear that 14.08.05 means 14 Aug 2005. The colour indicates the date of the experiment.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 18179, 2007.

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