

First, we would like to thank the reviewer for his/her valuable comments on the manuscript. We did our best to address all these comments and to summarize the changes made to the revised manuscript below.

Response to referee #2:

> *My major concern lies with the correction factor applied to account for deviations from pseudo-first-order kinetics.*

It's not entirely clear how the correction factor is determined for field data without full knowledge of the VOCs present? This is a significant disadvantage for this instrument given its aim is to provide the OH loss rate independently of knowledge of which VOCs are present in an air mass. All efforts should be made to ensure there is as little deviation from pseudo-first-order kinetics as possible.

As indicated in the original manuscript (P. 3826, l. 24-26 and P. 3833, l. 24-28), the correction factor applied on ambient measurements is an average value of individual correction factors derived from laboratory experiments for various gas standards. We have chosen these standards to cover the full range of reactivity encountered in the atmosphere (from ethane: $2.4 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ to isoprene: $10^{10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$). Therefore, averaging the correction factors derived for these various standards and using the variability observed within these correction factors as uncertainty for the averaged value allows factoring its dependence on the gas standard reactivity into its uncertainty. As mentioned in the supplementary material, this uncertainty is estimated to be 9% (see supplementary material S14) from the standard deviation of the correction factors derived for different gas standards within a restrained range of pyrrole-to-OH ratios (1.4-2.2), assuming that the pyrrole-to-OH dependence of F on this range of ratios is small (see Fig. 7 of the original manuscript).

> *What is the usual pyrrole:OH ratio used in ambient measurements for this and other CRM instruments? What are the limitations on increasing the ratio to ensure pseudo-first-order conditions?*

As shown in Fig. 7 of the original manuscript, the pyrrole-to-OH ratio varies usually between 1.6 and 2.2 (colored area) during ambient measurements for our CRM. This range of variations can be different for other CRM instruments. There are several drawbacks in using higher pyrrole-to-OH ratios. First, as it is shown in Fig. 3, a higher pyrrole-to-OH ratio leads to a larger artifact from NO, which is not desirable. Then, as stated in the original manuscript (P. 3830, l. 28- P. 3831, l. 1), higher pyrrole-to-OH ratios lead to lower OH mixing ratios in the reactor and therefore to smaller modulations between the different pyrrole signals (C1, C2 and C3), which in turn lead to higher detection limits. A tradeoff has to be found between the level of corrections to apply on the measurements and the detection limit. For our CRM instrument, a good tradeoff is to use a pyrrole-to-OH ratio in the range 1.7-2.0.

> *Page 3827, line 2 & Figure 7: What are the uncertainties associated with these parameters? How were the correction factors determined for the field measurements in the absence of complete knowledge regarding the VOC speciation?*

As mentioned above, an average correction factor is calculated from experiments performed using several gas standards and the dependence of this correction on VOC rate constants is factored into its uncertainty. The reactivity of these gas standards was chosen to cover most ambient air conditions. There is no need to know the composition of ambient air masses to apply this correction.

> Page 3828 onwards: If the model simulations are constrained to [pyrrole], [OH] and [VOC] how do simulated changes to [pyrrole] (i.e. simulated C1, C2 and C3) compare to experiments? i.e. if the model is run under the non-pseudo-first-order conditions of the experiment, are the simulations consistent with the experiments and thus in support of the arguments described for 'deviations from pseudo-first-order' conditions?

Simulations are constrained by initial concentrations of OH and pyrrole. OH concentrations are set in the model to reproduce the C1-C2 modulations. Therefore, simulated C1 and C2 are comparable to experimental values. The simulated C3 can be different from experimental values, which leads to the differences observed between simulated OH reactivity and measured OH reactivity for the experiments displayed in Figs. 6, 8 and 9 of the original manuscript.

> Page 3833, line 28: The recommendation for an average correction factor doesn't seem entirely appropriate as it would seem to require some knowledge of VOC speciation. It would be better to improve the sensitivity towards changes in pyrrole signal to allow instrument operation at higher [pyrrole] to give more confidence that measurements are truly under pseudo-first-order conditions.

See our responses above. There is no need to know the VOC composition of ambient air to apply this correction. We agree that working at a higher pyrrole-to-OH ratio would help to get closer to pseudo first order conditions and would lead to a smaller correction. However, as mentioned above, working at a higher pyrrole-to-OH ratio has also several drawbacks such as a higher limit of detection.

> Finally, describing the observations as a 'deviation from pseudo-first-order conditions' implies a reasonable expectation of pseudo-first-order conditions. Given the pyrrole:OH ratios reported, pseudo-first-order conditions should not really be expected, so it doesn't seem entirely correct to describe this phenomenon as a 'deviation', it would perhaps be better described along the lines of 'instrument operation away from pseudo-first-order conditions'.

As requested by the referee, the term "deviation from pseudo first order conditions" has been replaced by "not operating the instrument under pseudo first order conditions" all along the revised manuscript and revised supplementary material.

> My second major comment regarding this work relates to the modelling studies. The modelling work presented in the paper uses both a simple model and a more complex model based on the MCM. What is the residence time of gas inside the reactor? What is the extent of secondary chemistry in the reactor that is predicted by the models?

The residence time of gases inside the reactor has been estimated to be approximately 20s. Stable levels of pyrrole are observed in the simulations after a reaction time ranging from 50 to 400 ms, for both mechanisms, which is shorter than the residence time inside the reactor.

It seems that the use of both models is unnecessary. If there is sufficient time inside the reactor for secondary chemistry following the initial reaction with OH then the MCM model ought to be presented. If there is insufficient time in the reactor for any significant chemistry then the simple model, using rate constants for OH+VOC for each VOC present in the air

mixture, ought to be used. In general, it seems that the 'simple model' does not perform as well as the MCM-based model. While I can understand that the simple model may have been useful to the authors during instrument development, I don't feel that it adds anything of value to the manuscript. I would recommend removing the detail regarding the simple model to improve the clarity and readability of the paper.

The concomitant use of both mechanisms gives several interesting pieces of information. First, the observation that both mechanisms can correctly simulate the addition of gas standards inside the reactor showed that the secondary chemistry does not significantly impact the experimental observations. Then, simulations of the NO artifact using both mechanisms encompass the experimental observations (see Fig. 5 of the manuscript). This result indicates that differences between experiments and model is likely due to the secondary chemistry included in the mechanisms, such as the recycling of OH through propagation reactions involving NO, and leads to the conclusion that additional work is needed to investigate the pyrrole chemistry. Finally, comparing the results from the simple mechanism to the results from a mechanism similar to that used by Sinha et al. (2008) allowed showing the importance of cross- and self- reactions of radicals (see Fig. 8 and text P. 3829, l. 1-11). For these reasons we chose to keep the results from the two mechanisms in this publication.

> Abstract: The abstract is rather long and would represent the paper better if it were more concise, detailing only the points in this paper which are novel or covered in greater detail than is available elsewhere. In line 8, the OH reactivity is referred to as the 'loss rate of ambient OH', when it is the rate coefficient describing the loss, not the loss rate itself. The use of terms such as 'promising' (line 9) should be avoided.

As suggested by the referee, the abstract has been rewritten to present what is covered in greater details in this publication. Please see the responses made to reviewer 1. The terms "first order loss rate" and "promising" have been removed.

> Page 3805, line 4: '... reproducing ...' to '... reproduction of...'

> Page 3806, line 8: '... suit ...' to 'suite'.

The requested modifications have been made.

> Page 3807, line 4: Please provide some brief detail regarding alternative techniques and why the CRM is potentially advantageous. Hansen et al. (2015) is a poor reference for the pump-probe technique (largely because it is as yet unpublished), please provide the original references describing the techniques.

The original publications describing the alternative techniques have been included in the revised manuscript: Kovacs and Brune (2001) and Sadanaga et al. (2004) for the total OH loss rate method and the pump and probe method, respectively.

The main advantages of the CRM technique are indirectly given in the original manuscript (P. 3807, l. 6-7). This technique does not require direct OH measurements, which are difficult to do and expensive, and does not require highly skilled operators. In addition, the small sampling flow rate of CRM instruments (a few hundreds of SCCM) compared to TOHLM and Pump-Probe instruments (a few SLPM) allows extending its use to small chambers and cuvette experiments. This additional advantage has been mentioned in the manuscript.

> Page 3807, line 27: Why ‘intercompared’ and not just ‘compared’?

“intercompared” has been replaced by “compared”.

> Page 3808, line 5: ‘... exception made of two studies ...’, please rephrase to improve clarity, does it mean ‘except for two previous studies’?

“exception made of two studies” has been replaced by “except for two previous studies”.

> Page 3808, lines 13-15: Details of previous deployments of this instrument are not currently available to the reader, please provide some details of the initial setup if results are presented in this work using an earlier design.

> Page 3810, lines 23-25: See earlier comments regarding the paper by Hansen et al. Please provide some details regarding the original setup, what problems were observed and how improvements have been made in the current setup.

The article of Hansen et al. is now available in AMTD: Hansen, R. F., Blocquet, M., Schoemaeker, C., Léonardis, T., Locoge, N., Fittschen, C., Hanoune, B., Stevens, P. S., Sinha, V., and Dusanter, S.: Intercomparison of the comparative reactivity method (CRM) and pump-probe technique for measuring total OH reactivity in an urban environment, Atmos. Meas. Tech. Discuss., 8, 6119-6178, doi:10.5194/amtd-8-6119-2015, 2015

> Page 3809, line 6: ‘details’ to ‘detail’. Again, the paper by Hansen et al. (2015) is not currently available, if it contains relevant details to this work please provide a brief description.

> Page 3810, line 10: ‘technic’ to ‘technique’.

> Page 3810, line 16 (and elsewhere): ‘pseudo-first-order’ is generally preferred over ‘pseudo first order’.

> Page 3811, lines 21&23: ‘than’ to ‘as’.

> Page 3812, line 20 (and elsewhere): ‘applied on’ to ‘applied to’.

> Page 3812, line 25: ‘on a large range’ to ‘over a large range’.

> Page 3813, line 5: ‘which levels’ to ‘levels of which’.

The requested modifications have been made.

> Page 3814, line 6: See previous comments. What is the limitation that prevents increasing the pyrrole to OH ratio? What are the ratios used in other CRM instruments?

See our replies above and replies made for the first reviewer.

> Page 3814, line 21: It is unnecessary to describe the model as both zero-dimensional and as a box model, one implies the other.

“zero dimensional box model” has been replaced by “zero dimensional model”.

> Page 3815, line 16 onwards: How representative is the rate constant used for OH+VOC? Are [VOC] scaled accordingly to give the expected OH reactivity?

The reaction rate constant chosen for the surrogate hydrocarbon has been arbitrary set to $5.0 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. This value is typical for C5-C6 alkanes or aromatic compounds

such as toluene. This has been indicated in the revised manuscript. The [VOC] has been initialized in the simulations to give the requested OH reactivity.

> Page 3815, line 19: *Is the IUPAC 2001 recommendation the most recent? I think there have been more recent recommendations*

We agree with the referee that more recent recommendations exist. However, the rate constants for inorganic reactions used in the simple mechanism are similar to the values used in MCM v3.2, except for three reactions:

(1) The quenching of $O(^1D)$ is 10% slower in the simple mechanism

(2) The reaction of $O(^1D)$ with water to produce two OH is 3% slower in the MCM mechanism

Nevertheless, ozone photolysis was set at zero for these simulations and $O(^1D)$ was not constrained in the model. Therefore, the differences observed for these 2 reactions do not impact the simulations.

(3) The reaction of HO_2 with NO, responsible for the NO artifact, is 5% slower in MCM.

We have performed additional simulations using the simple mechanism and the MCM reaction rate constant for HO_2+NO . The results are shown in Fig. R1. When we compare the new simulations to those presented in the original manuscript, we only observe a small decrease of ΔC_3 (0.7-2%) for the three pyrrole-to-OH ratios.

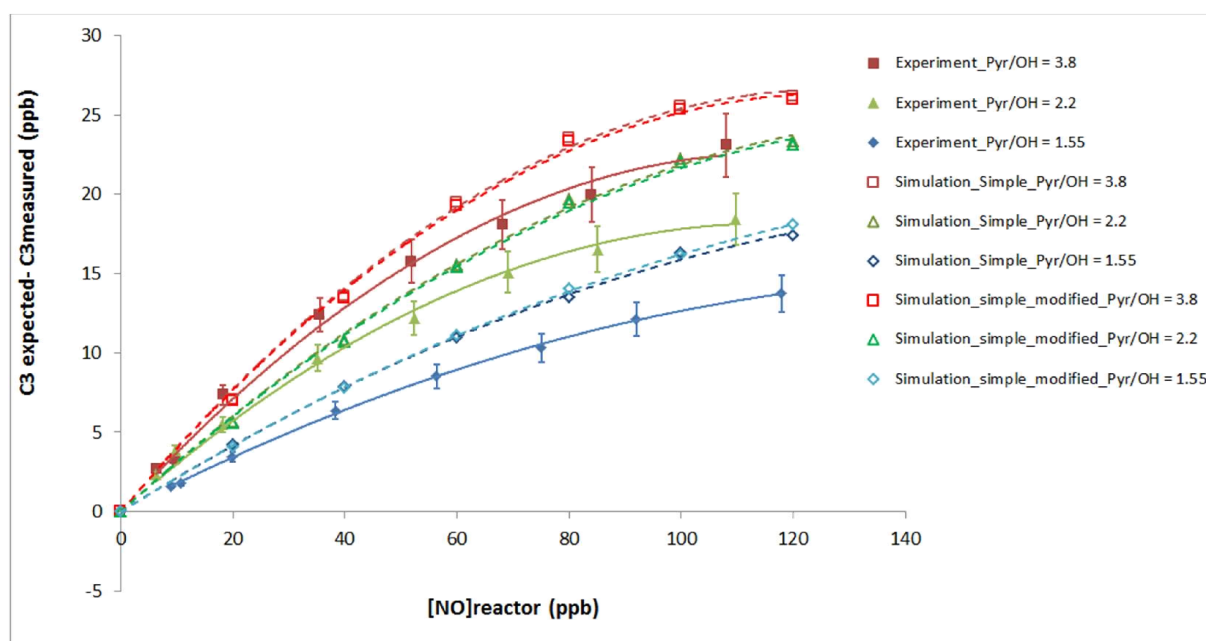


Figure R1: Comparison of laboratory observations to model simulations for the NO artifact at various pyrrole-to-OH ratios. Experimental (filled symbols and solid lines) and simulated (open symbols) results. The dashed and dotted lines are for the Simple Mechanism and the updated Simple mechanism, respectively.

To conclude on the use of more recent recommendations for inorganic reactions in the simple mechanism, this update would lead to negligible changes for the simulations presented in this publication and would not impact the conclusions. We have, therefore, decided to keep the simulated results presented in the original manuscript using recommendations from IUPAC 2001

> Page 3816, line 27: *What is the sensitivity of the model output to this rate constant?*

This rate constant has been set to this value as recommended by Atkinson et al. (1984) and Dillon et al. (2012). No sensitivity test has been performed for this rate constant but it would certainly lead to significant changes in the simulated results since it will directly impact the simulated C2 and C3 levels. In addition, this rate constant is also used to calculate the measured OH reactivity.

> Page 3817, line 10: *Give the range of observed NO and NO2 concentrations.*

The requested information has been given in the revised manuscript:
“(Moderate to high NOx: 1-150 ppb)”

> Page 3818, line 15, Figure 2: *What are the slopes of the individual datasets in Figure 2? What are the uncertainties in the fits?*

The linear regressions for the individual datasets have been added in Fig. 2 in the revised manuscript. Uncertainties on the slopes and intercepts have also been added. Uncertainties range between 6-26% for the slopes and 2-8% for the intercepts.

> Page 3818, line 17: *‘Black’ to ‘black’.*

> Page 3818, line 19: *‘apply on’ to ‘apply to’.*

The requested modifications have been made.

> Page 3819, line 22: *What is the impact of forcing the origin through zero? How does it affect the fit if allowed to vary?*

Not forcing the origin through zero leads to intercepts ranging from 0-0.9 ppbv and to relative changes in the regression coefficients ranging from 0 to 15% for the 2nd order monomial and 0 to 12% for the 1st order monomial.

However, the y-axis represents the difference between expected and measured C3 levels due to OH recycling inside the reactor. The expected C3 is calculated by adding the expected rise in pyrrole due to the reactivity of NO with OH to the C3 mixing ratio that was measured without NO. Without NO inside the reactor this expected C3 would then be equal to the measured C3 and the difference of these two variables would be zero. We do believe that it is better to force the origin of the fit to zero to improve the reliability of this correction.

> Page 3823, lines 5-8: *Changes in C3 owing to changes in radical concentrations and radical reaction rates could be demonstrated unequivocally using the model simulations. It would be helpful to show such simulations to provide support for the argument given here.*

To demonstrate that the spurious OH formed from HO₂ + NO will preferentially react with pyrrole rather than HO₂ at a higher pyrrole-to-OH ratio, we tracked how much OH was formed through HO₂ + NO (F_{HO₂+NO}) and how much OH reacted with HO₂ (F_{OH+HO₂}) during the simulations. To do so, we included flags in the model for these two reactions. Figure R2 shows the ratio between these 2 quantities (F_{HO₂+NO}/F_{OH+HO₂}) as a function of NO. From this figure, it is clear that F_{HO₂+NO}/F_{OH+HO₂} is higher at higher pyrrole-to-OH ratios, indicating that the proportion of OH, formed via reaction of HO₂ with NO, and reacting with HO₂ is lower at higher pyrrole-to-OH ratios. This result indicates that the spurious OH reacts preferentially

with pyrrole when the pyrrole-to-OH ratio is increased, causing a higher change in C3, and hence a larger artifact.

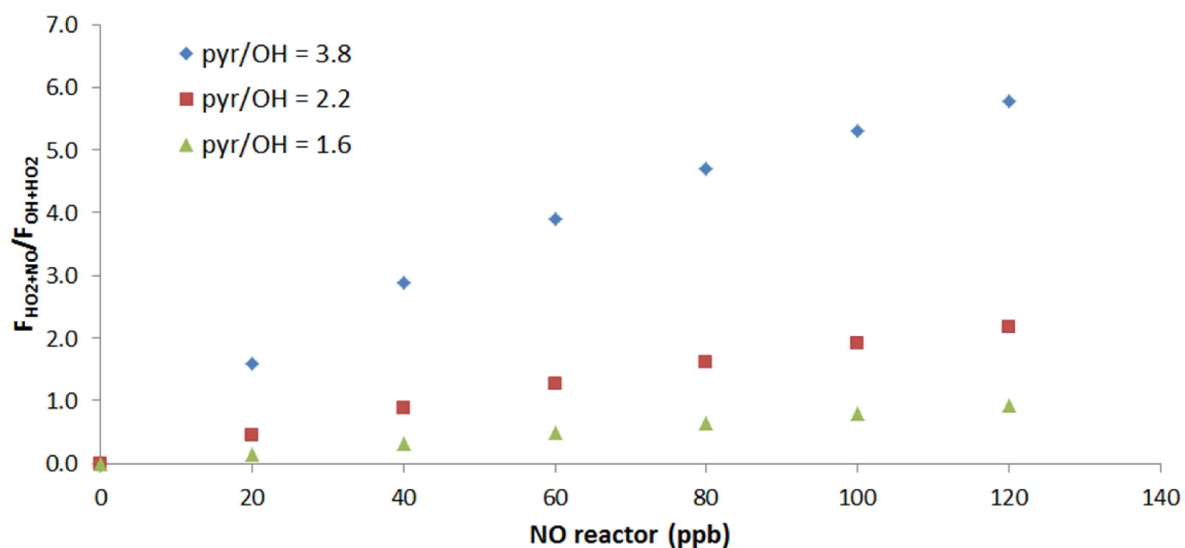


Figure R2: Trend of $F_{\text{HO}_2+\text{NO}}/F_{\text{OH}+\text{HO}_2}$ with NO for different pyrrole-to-OH ratios (1.6, 2.2, 3.8)

- > Page 3823, line 21: 'to reproduce' to 'for reproduction of'.
- > Page 3824, line 13: Lower case 'i' and 'e' for isoprene and ethane.
- > Page 3824, line 28: 'O¹D' to 'O(¹D)'.
- > Page 3830, line 18: 'considering' to 'to consider'.

The requested modifications have been made.

- > Page 3824, line 2: What is the potential for formation of OH from photolysis of oVOCs?

As stated in section 2.2 of the original manuscript, the photolysis of several OVOCs has been estimated to be less than 1% (see P. 3811, l. 5-10). As a consequence, the formation of OH from OVOC photolysis is likely negligible.

- > Page 3830, line 18: Why can the model simulations reported here not include a constant source of OH?

The inclusion of a constant source of OH would require a more complex approach such as simulating the flow dynamic inside the reactor. Such approach will be investigated in a future study.

- > Figure 1: Please highlight the inserted graphic in some way to make it stand out more from the main diagram.

The insert has been framed in the revised manuscript for a better visibility.

- > Figure 2: Please provide the fits to the individual datasets shown as well as the average, with uncertainties given for the fits.

The requested modifications have been made.

> *Figure 3: What are the uncertainties in the fit parameters? The lower panels are a little small to read. Be clearer about what is being plotted/fit in the lower panels – the fit parameters in the equations in lower panel should be consistent with those in the upper panel (i.e. avoid $y = ..$ and use $a = ...$ for the left panel and $b = ...$ for the right panel, x is also different between the upper and lower panels so please use different symbols). Please change ‘monomials’ to provide a clearer description in terms of the parameters a and b in the upper panel. Likewise for Figure 5.*

Uncertainties for the fit parameters of the top panel in Fig. 3 have been added. The lower panels have also been re-sized to be more readable. The parameters used in the different equations have also been changed for consistency (i.e., y replaced by a or b etc...). Similar modifications have been made for Fig. 5.

> *Figure 7: See earlier comments regarding determination of the correction factor for field data. What are the uncertainties on the best-fit line? How do these impact the final reported OH reactivity?*

See responses above. The uncertainty associated to the determination of an average correction factor has been described in the supplementary material S14 and is estimated to be 9%.

> *Figure S1: Most ambient data will be lower than the lowest measured reactivity shown on these plots, were any experiments performed at lower reactivities? What are the intercepts of these plots? What was the pyrrole:OH ratio for these experiments? How was the correction for the deviation from pseudo-first-order kinetics determined? How large were the corrections?*

We agree with the referee that most ambient data will be lower than the lowest measured reactivity shown on these plots. However, given the concentrations of the different compounds in each mixture (several ppm, see table S1), there were difficulties to get lower OH reactivity values keeping the current experimental flow conditions in the reactor. The regression lines were forced by zero. Not forcing the origin by zero leads to intercepts that are not statistically significant (uncertainties greater than the intercepts themselves)

The pyrrole-to-OH ratios were 1.8 and 1.9 for the OVOC and HC experiments, respectively. This information has been added in Fig. S1 of the revised supplementary material.

The measured OH reactivity values were corrected for not operating the instrument under pseudo first-order conditions using the procedure described in the main paper, i.e using an average correction factor. These corrections were approximately 15%.

> *Figure S7: Missing ‘x’ in several of the rate constants listed. Also for Figure S9.*

The requested modifications have been made.

> *Supplementary material section 9&11: If inclusion of these additional reactions does not help to reconcile the simulations with the measurements does it not imply that the correction factors should actually be larger than they have been reported to be?*

As indicated in the original manuscript, we rather think that the differences may be due to a potential lack of knowledge in the pyrrole chemistry or an impact of the flow dynamic inside the reactor (see P. 3830, l. 12-15).

It is important to note that this result highlights that correction factors should be based on experimental determinations and that model-derived corrections should be avoided if possible.

> *Figure S12: Does ‘modified MCM’ refer to just the inclusion of 200 ppb in the initial conditions or has the mechanism itself been modified in some way*

No modification was made in the mechanism and we just started the simulations with 200 ppb of ozone. The term “modified” has been removed for clarity in the revised supplementary material.

> *Supplementary material section 14: ‘since the statistic for ...’ to ‘since the statistics for...’.*

The requested modification has been made.

> *Should the reported uncertainties in F include some comment on additional unquantified uncertainties owing to incomplete knowledge of VOC speciation?*

See responses above.

References

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