Atmospheric
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Discussions

Interactive comment on "Detailed characterizations of a Comparative Reactivity Method (CRM) instrument: experiments vs. modelling" *by* V. Michoud et al.

Anonymous Referee #2

Received and published: 19 May 2015

Review of "Detailed characterizations of a Comparative Reactivity Method (CRM) instrument: experiments vs. Modelling", V. Michoud et al., Atmos. Meas. Tech. Discuss., 8, 3803-3580, 2015

The authors present a thorough description of the characterization of a new instrument at Mines Douai using the Comparative Reactivity Method (CRM), and report a comprehensive series of laboratory tests to characterize interferences and instrument performance alongside model calculations used to support and interpret the experimental observations. While the technique itself is not new, and the interferences are, for the most part, previously described in the literature, the details regarding the cor-

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rections derived to account for interferences are likely to be of interest both to other groups using and developing CRM instruments and to groups interested in assessing measured OH reactivities. The manuscript is within the scope of AMT and I recommend publication once several comments, listed below, have been addressed.

Major comments:

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.

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?

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?

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?

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.

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'.

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? 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.

Minor comments:

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.

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

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

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.

Page 3807, line 27: Why 'intercompared' and not just 'compared'?

Page 3808, line 5: '... exception made of two studies ...', please rephrase to improve clarity, does it mean '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 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 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.

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'.

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?

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

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?

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

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

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

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

Page 3818, line 17: 'Black' to 'black'.

Page 3818, line 19: 'apply on' to 'apply to'.

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

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.

Page 3823, line 21: 'to reproduce' to 'for reproduction of'.

Page 3824, line 13: Lower case 'i' and 'e' for isoprene and ethane.

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Page 3824, line28: 'O1D' to 'O(1D)'.

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

Page 3830, line 18: 'considering' to 'to consider'. Why can the model simulations reported here not include a constant source of OH?

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

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

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 'mononomials' to provide a clearer description in terms of the parameters a and b in the upper panel. Likewise for Figure 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?

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?

Figure S7: Missing 'x'in several of the rate constants listed. Also for Figure S9.

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?

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?

Supplementary material section 14: 'since the statistic for ...' to 'since the statistics for...'. Should the reported uncertainties in F include some comment on additional unquantified uncertainties owing to incomplete knowledge of VOC speciation?

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3803, 2015.

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