

General Comments:

The paper by Yang et al. reports CRM OH reactivity measurements conducted in two Chinese cities : Beijing in August 2013 over a 17 day period and in Heshan between 19 Oct – 22 Nov 2014. Using the measured datasets and a zero dimensional box model, the authors investigate the source of missing OH reactivity in Beijing (21%) and Heshan (32%) and also calculate the ozone production efficiency (defined as ratio of ozone production rate/ NO_x production rate). They conclude that the ozone production efficiencies (OPE) would be significantly underestimated at both sites (by 27% in Beijing and 35% in Heshan), if the OPE were not constrained by the measured OH reactivity. Hence they conclude that OH reactivity measurements are necessary for accurate determination of ozone production efficiencies.

The paper is interesting and has attempted deployment of the CRM technique in very challenging high NO_x concentration environments. Such a study would certainly be of great interest to the ACP readership from the perspective of fundamental process based understanding of OH reactivity and ozone production at two important sites in China. The efforts of the authors ought to be appreciated from this perspective and the study could be a valuable addition to the literature. However, there are some major technical concerns concerning the quality of the measurements and analyses, which need to be clarified/addressed/corrected by the authors before one can have confidence in the dataset and conclusions. The presentation and language also needs to be improved before it can be considered suitable for publication in ACP.

Major Concerns:

- 1) **OH reactivity measurements:** The authors have provided a good qualitative description of the CRM measurement system, but this description is generic for the CRM technique. In order to assess the quality of the measurements, relevant technical information pertaining to the operating conditions must also be provided. For example: What was the pyrrole /OH concentration ratio inside the CRM reactor during these measurements? Did it change between the deployments? What were the typical pyrrole concentrations for the C₂ , C₀ and C₁ stages? What was the dilution factor

for ambient air inside the reactor (i.e. flow of syn air/amb air to total flow)?
What was the residence time of air inside the reactor?

It appears that numerical simulations for calculating deviations from the first order conditions were neither carried out nor applied. Why? While it is good that the authors tested the accuracy of the system using propene, propane and a hydrocarbon mixture, it can be seen from the results (Figure 2) that the slopes obtained are rather different for propene (1.31) Vs propane (0.93 to 1.04). If the pyrrole (C1 concentration) /OH (C1-C2 concentration) ratio was different in these calibration experiments, it could explain the same and then correcting for the deviations from first order conditions for the relevant pyr/OH ratio, would ensure better accuracy and take into account correction factors for each type of standard.

2) NO-correction experiments: Figure 3: The results are rather strange. From the paper it is not clear whether the NO concentration shown on the x axis are the ambient NO concentrations or the NO concentration inside the CRM reactor after dilution. The authors state that they have used the former (Lines 177-179; Page 6). This would be inappropriate to use considering the non linearity of NO_x-VOC chemistry for OH formation. Instead corrections are valid only for NO concentrations inside the reactor.

I am also puzzled that the correction factor (Δs^{-1} on y axis) is the same in magnitude for $60 s^{-1}$ of OH reactivity as well $120 s^{-1}$ of OH reactivity at the same NO concentration. The NO correction should logically be lower at $120 s^{-1}$, as the additional reactivity would compete with NO more efficiently for the HO₂ resulting in lowering the OH formation due to NO + HO₂. A simple numerical simulation would reveal the same. At the large NO concentrations observed during their deployments (> 10 ppb NO), it is difficult to trust that the highly non linear secondary chemistry effects arising from NO + RO₂ and NO + HO₂ or even HONO photolysis inside the reactor can be accurately corrected. Note that the secondary chemistry is also occurring in a mixture containing ambient air that has several reactive compounds that have different chemistry from the standard mixtures used and some of the compounds are even unknown. In such scenario, relying on calibrations involving just propane or propene or a mixture of few

compounds cannot yield robust correction factors at high NO concentrations. For the high NO concentrations and OH reactivity conditions encountered in the present study, the authors should have used the flexibility of the CRM method in terms of adjusting the dilution factor of ambient air inside the CRM reactor. They could have then ensured that the NO concentrations were at most few ppb inside the CRM reactor, keeping the effect of NO induced secondary chemistry and its magnitude much lower. In the context of the present study, applying corrections that maybe at times 100% or even higher in magnitude relative to the uncorrected OH reactivity measurements is rather disconcerting. It renders most of the reported OH reactivity a function of the correction factor! This effect is apparent in Fig 5 a and 5 b, when one looks at the correlation between the time series of NO and the corrected measured OH reactivity shown in the graph. The authors need to discuss this issue more comprehensively. In this regard, correlation plots of the measured OH reactivity (y axis) Vs the NO concentration (x axis) and the missing OH reactivity Vs NO concentration at both sites using the temporal data (5 or even 10 min averages would do), would help much to shed light on the above point. Also, it would be good to add the time series of calculated OH reactivity to Fig 5 a and 5 b for an idea of temporal variations in both the measured OH reactivities and calculated OH reactivities. At present only few days of time series data from both sites have been presented in Fig 11 and Fig 12.

The authors may also wish to consider excluding the ambient OH reactivity data for periods when the NO concentrations lead to corrections of the same magnitude as the uncorrected OH reactivity data (100% or more). In that case, the present findings of unexplained OH reactivity may need to be revisited. At the very least, suggestions on how to perform the CRM measurements better in high NO_x environments can be an outcome of the present study.

- 2) **NO₂ measurements and ozone production efficiency calculation in model using calculation NO₂:** The authors mention (Lines 221-223; page 8) that the NO_x measurements were performed using the chemiluminescence technique (Instrument Model 42i, Thermo Fischer Inc., U.S.). If this is the case then obviously their NO₂ measurements would suffer from

a positive bias (see for e.g. Reed et al. 2016; Atmos. Chem. Phys., 16, 4707–4724, 2016) due to interference from organic nitrates, nitrous acid (which the authors report was quite high during their study without showing the actual temporal data) and nitric acid. The magnitude of such differences in inter-comparison studies involving more specific NO₂ instruments have been shown to overestimate the NO₂ concentration by upto 400% during the daytime (see Chapter 2 by Kleffman et al. in Disposal of Dangerous Chemicals in Urban Areas and Mega Cities, NATO Science for Peace and Security Series C: Environmental Security, I. Barnes and K.J. Rudziński (eds.), DOI 10.1007/978-94-007-5034-0_2, # Springer Science+Business Media Dordrecht 2013. The authors mention that they used the measured NO₂ to constrain the model (lines 246-248; page 9). If the measured NO₂ is significantly in error (say 50%), how would it affect the results of their analysis keeping in mind the implications for the unexplained OH reactivity and the calculation of the ozone production efficiency using $P(\text{NO}_2)$ (Equation 2-3). This could affect their conclusions majorly and the authors should address this concern.

OTHER COMMENTS:

Abstract:

(Line 22; Page 1) and elsewhere in the paper: The authors should report the measured OH reactivities and other concentration measurements by rounding off to significant figures.

(Line 34; Page 2): English is wrong: “...was presumably attribute to oxidized species...”

Introduction:

Equation 1-1: The concentration is expressed as small $[x_i]$. Please replace by capital X_i as in subscript here and elsewhere.

Line 46, page 2: should be “reactive” instead of “reductive”

Lines 50-61: The authors should include other more recent relevant measurements of OH reactivity from another suburban site in Asia in Table 2, reported by Kumar, V et al., Int. J. of Mass Spectrom., 374, 55-63, 2014.

Line 108; Page 4: Although Yang et al. 2016 is cited, Sinha et al., 2012 were the first to outline this approach and use it for determining ozone production regimes.

Line 125-126; Page 5: Mention the inlet residence time. What sorts of inlet filters were used? How often were they changed under such polluted conditions?

Line 159-164; Page 6: Humidity adjustments to synthetic air for matching ambient humidity changes: It is difficult to imagine how the simple needle valve contraction can dynamically track and adjust to the ambient humidity. Some data showing the m39 water cluster concentrations of the PTR-MS for the C2 and C3 stages would be helpful.

Line 167; page 6: Spelling error: “genrated”

Lines 185-201: HONO interference: The authors do not show or mention anywhere the actual HONO concentration measurements. Considering that the OH concentration inside the CRM reactor is typically several tens of ppb, it is difficult to understand how typical ambient HONO concentrations of few hundred ppt can cause a significant interference, through the mechanism outlined by the authors. At this stage I am beginning to wonder if the authors have a fair assessment of what goes on inside the CRM reactor.

In general, the figures, their captions and legends need to be improved.

In the supplement Tables S3 & S4 are identical except for the captions!

In the supplement Tables S5 and S6 are identical except for the captions!

Section 2.3.1: How is the dilution accounted for in the model? What is the model estimated concentration of PAN and its production rate? The latter would have bearing on their assumption of approximating $P(\text{NO}_z)$ as $P(\text{HNO}_3)$

Section 3.1: lines 270-273, Figure 5-a: During some periods (e.g. evening of 17-08-2013 and 24-08-2013) CO mixing ratios are close to zero in Beijing. How can one have trust in such measurements?

Section 3.1: Figure 5-a: There seems to be negative mass concentration of PM_{2.5} on 17, 19, 23, 25 and 26 October evening which are masked because the axis starts from zero. Please explain.

Figure 6 : I cannot make out much as it is difficult to read as the Figure legends are hardly legible. There does not seem to be much difference between the peak NO/NO₂ ratios between Beijing and Heshan. Then how can one be sure that Heshan is influenced more strongly by transported air masses (see Lines 301-303)? Please clarify.

L 317 and 319: The unit of OH concentration should be molecules cm⁻³ (and not mole cm⁻³). Similarly in L314 and 316, mole should be replaced by molecules.

Figure 7 a and b: Please mention what the red dotted lines and shaded regions signify?

Figure 8: Use appropriate legends? Not clear what is meant by “*reac_mea_median*”

L338-340: For Heshan, another pollution episode can be observed on 5th November despite lower CO, NO_x and other pollutants. Please mention that too.

L348-352: Reasoning is not clear:

This contradicts the previous statement that Heshan receives more aged airmasses. Aged airmasses should also show more contribution from OVOCs. Moreover if faster photo-chemical production during August in Beijing, is really the reason, then one would expect less contribution from primary hydrocarbons in Beijing and more contribution of primary hydrocarbons in Heshan.

L 425: Please provide the major contributors among unmeasured aldehydes.

L437 and Table S5 and S6: Please provide full name of “ALD”, GLY+MGLY”, “ISOP” and “DCP” at-least once. As mentioned in the text, HCHO is a measured species. Please provide the value of k_{cal} due to HCHO in table S5 and S6 also for comparison.

Section 4.3: Please mention the range of OPE or an average OPE in the text also to provide an estimate of number of ozone molecules produced per molecule of NO_x consumed.

Lines 464-469: The argument is circular:

First the authors assume that the missing reactivity is due to alkenes and OVOCs which have high ozone production potential. Next the model is constrained by the “assumed” species in the second scenario. Obviously these species will provide extra ozone production.

The LOD reported for the CO, NO_x and O₃ instruments in the supplement are much less than what is claimed by the instrument manufacturers in their manuals (40ppt for NO_x, 1ppb for O₃ and 40ppb for the 48i trace level enhanced CO analyzer). Please provide the details of how you obtained a lower LOD for these instruments or correct the Table in the supplement.