Reply to Reviewer's comments

General Comments

This paper presents OH reactivity measurements in Beijing and Heshan, China using the CRM technique. Missing OH reactivity was found in both studies and impact on ozone production efficiency was assessed using a box model. The scope of this work is important and can improve our understanding of ozone production and I think this work is worth publishing. My big concern is the uncertainty in the OH reactivity measurement, which may reduce the significance of missing OH reactivity on the ozone production. Another concern is that in the ozone production efficiency (OPE) calculation, the NO_x *loss due to organic nitrate formation is omitted, i. e., only the formation of nitric acid from OH+* NO_2 *is considered. This could overestimate the OPE depending on the relative importance of organic nitrate production over nitric acid production in these two environments. Overall I found the manuscript needs much improvement in English. The authors need to clarify many things in several parts of the manuscript (See Special Comments below), especially the discussion of the effect of the measurement uncertainty on importance of missing OH reactivity and the clarification on how the measurement corrections was done due to interference of humidity and NO. In addition, I would ask the authors to consider the following special comments in their revision.*

Response: Thank you for your commendation and appreciate for your questions and suggestion. Specially the two major concerns about the measurement uncertainty and the OPE calculation. For the measurements uncertainty, I made some clarification about the measuring setups as well as some explanation about the correction methods, following all the reviewers' comments. Hopefully this manuscript would help you to trust the validation of the method. For the OPE calculation, your advice is so helpful that we really missed the organic nitrate formation part, which would surly influence the results significantly as you have suggested. So in the new manuscript, we re-calculated the OPE and achieved new results.

Special Comments:

1. L.2: The country should be added, i.e. "Case studies in Beijing and Heshan, China"

Response: Accepted and modified following the suggestion.

2. L.22-23: with a detection limits of 5 s^{-1} *stated in L. 198, it is not possible that two decimals in the OH reactivity values can be significant. Integer numbers probably enough.*

Response: Accepted and modified following the suggestion. However, this should be discussed, as in this method, the final results were achieved by the equation (2-1). The choice of the significant figures should be made depending on how well the experimental method can tell the difference in two close reactivity. However, this was not discussed in this manuscript. In this one, we accept the comments.

3. L23: it should read "Measurements in Beijing presented…"

Response: Accepted and modified as "The data in Beijing showed".

4. L25-26: need to define missing OH reactivity here. I can guess it is the different between measured OH reactivity and OH reactivity calculated from measured OH reactants. If so, state so.

Response: Accepted and modified as suggested. Appreciate the suggestions.

5. L32:"However, the model failed to explain the missing reactivity in Heshan", but was the box model able to explain the missing OH reactivity in Beijing?

Response: The question was a good one. We can only say in the case study between August 16th and 18th, 2013. The model was able to explain the missing reactivity in daytime. But for other periods or in the evening, it could not work well.

6. L35-36: it should read "...when the model is constrained by the measured reactivity ..."

Response: Accepted and modified following the suggestion. This should be as you said. Thank you.

7. L48: remove "researches" or change it to "calculations".

Response: Change it to "calculations" as suggested. Appreciate that.

8: L70: "... the 75% missing reactivity in Paris in MEGAPOLI under continental air masses influences", need a reference for this statement. It should be mentioned that missing OH reactivity in each study depends heavily on the completeness of measurement suite, especially VOCs species, so the next paragraph can follow.

Response: Accepted and add the reference. The detail about the VOCs species measured in these campaigns are listed in table 1 and table 2. This was really important that the defined missing reactivity were really dependent on the measuring suite.

9. L89-90 change " in one case could increase reactivity by over 50%..." to " ... in one case which could increase reactivity by over 50%..."

Response: Accepted and change to "… in once case the OVOCs could increase reactivity by over 50%..." It should be clarified here we were talking about the importance of OVOCs in reactivity. Appreciate your suggestions.

10. L91. An increasing concern.

Response: Accepted and change it to "Ground-level ozone pollution has been of increasing concerns in China".

11. L92: What is the ozone level for Grade II of China National Ambient Air Quality Standards?

Response: Sorry to fail to present the standards. So add "(93 ppbV)" after the "Grade II of China National Ambient Air Quality Standards (2012)".

12. L94-95: "… it appears there is an increasing trend for ozone in Beijing and other area…" for what time frame? Recent years?

Response: Appreciate the question. It was observed the increasing trend for recent years. As presented in Zhang et al, 2014, there was observed an increasing trend in one Beijing site between 2005 and 2011.

13. L104: change those to which.

Response: Accepted and change the sentence to "Due to the limitation of current measurement techniques, some VOCs species which could not be quantified so far, and therefore cannot be integrated into current chemical mechanisms of model run, could laid a great uncertainty in ozone production prediction".

14. L106: from the total OH reactivity.

Response: Accepted and change as suggested. Thanks for this advice.

15. L109: change "… two intensive observations datasets conducted …" to "… data from two intensive field studies conducted"

Response: Accepted and modified as suggested.

16. L114-116: consider to change this sentence to "The possible missing reactivity and its importance for the ozone production calculation are discussed"

Response: Accepted and modified as suggested.

17. L124-126: consider to change this to "a 14.9 m Teflon inlet with an outer (I assume) diameter of 3/8 inch…"

Response: Accepted and change to "Ambient air was sampled after a teflon filter and then pumped through a 14.9m Teflon 3/8 inch (outer diameter) inlet …"

18. L136: Some impurities in dry air and nitrogen could also be photolyzed.

Response: This could be true. So we also did one experiment in C0 and C1 mode but without pyrrole. We observed no significant difference in m/z 68 signals. So we assume the photolysis of impurities in dry synthetic air and nitrogen would not directly cause influence on pyrrole measurements. But this question was important. Appreciate for the concern.

19. L142-143: total ambient (?) OH reactivity is calculated as…

Response: Accepted and change it to "total OH reactivity of ambient air …"

20. In Fig.2, the color for symbols with different standards is not clearly shown. Consider to use different symbols and/or change to different colors for symbols and lines with a better color contrast.

Response: Accepted and modified the figure as suggested.

21. L155-156: What is the "uncertainty range for all calibrations"?

Response: It means the correlation factors were within certain range taking all factors, such as the uncertainty from standard gases, the mixing into consideration.

22. L157-165 about correction due to humidity: it is not clear how exactly this correction was done based on Figure S2, where no labels for x and y axes are given so we really do not know what is plotted here. If the pyrrole signal versus relative humidity are plotted, why there are negative values?

Response: Sorry for the unclearness of the axis labels. The x axis represents delta m/z 37 signals, and the y axis represents delta normalized m/z 68 signals. We chose a medium relative humidity as the "zero" point. We got the S_{37}^0 and S_{68n}^0. Then we got the delta m/z 37 signals and the delta normalized m/z 68 signals as follows:

$$\text{delta m/z 37 signals} = S_{37}^i - S_{37}^0$$

$$\text{delta normalized m/z 68 signals} = S_{68n}^i - S_{68n}^0$$

23. L166-182 about the correction due to NO: in Fig. 3 the y axis is labeled as delta reactivity. Is this the difference between calculated (standards) and measured OH reactivity? In the legends of the figure, there are reactivity numbers (60/120/180 s $^{-1}$) and I assume these are based on the reactivity calculated from the contents in the standard gases. If this is correct, why can the delta reactivity be 300 – 600 s^{-1}? As stated in L. 173-174, the "measured" reactivity decreased as the NO mixing ratio increased. If so, the measured OH reactivity should be lower than the calculated values and the *difference should be also less than these numbers (60/120/180 s* $^{-1}$*). Please clarify.*

Response: Thanks for the question. This was a tricky part for the explanation of "delta reactivity". The delta reactivity is defined as the difference between "measured" reactivity and "calculated" reactivity. However, this "measured" reactivity is derived from calculation of the m/z 68 signals, which equals the calculated reactivity in campaign observations. The "calculated" reactivity is actually the standard reactivity calculated from the mixing ratios of standard gases and rate coefficients, which equals the measured reactivity in campaign observations. This is a little confusing. Normally, the "measured" reactivity in NO correction experiments were lower than the "calculated" reactivity due to the OH radicals generated from NO recycling.
The delta reactivity could be even larger than the standard reactivity. This is because due to the excessive OH radicals generated from NO recycling, c3 could be even lower than c2 and negative values of "measured" reactivity could be calculated from the equation 2-1.

24. L.192-193: Was the correction associated with HONO interference also applied to the measurements in both sites, or to the measurements in Heshan only, since it looks like there is no HONO measurements in Beijing from Table S1.

Response: Thank you for your suggestions. Yes we only used the HONO correction in Heshan datasets. One reason is we didn't have the HONO measurements in August 2013 in Beijing. The other reason is from later measurements in Beijing, we found the HONO levels in summertime in PKU site was much lower than the results from Heshan. So we did not apply the correction in Beijing.

25. L.198: 2σ instead of 2δ.

Response: Appreciate your suggestion very much. Modified as suggested.

26. L.198-201: is the uncertainty of 20% for 1σ or 2σ? Shouldn't the uncertainty associated with NO correction be taken into account?

Response: Thanks for your question. The uncertainty of 20% is for 1σ. This is the total uncertainty for ordinary measurements. The uncertainty associated with NO correction is largely depended on the NO mixing ratios. However in our NO correction experiments, we calculated the uncertainty between 10%-15% (1σ).

27. L.248-251: it is not clear what output results from the box model was used in the calculations, time dependent results or stead-state result? The authors mentioned both a time-dependent mode of 5 min and stead-state conditions with a 3-day spin-up time. Please clarify.

Response: Thanks for the question. For the model we were used in this work, the model was operated in a time-dependent mode, but we need a 3-day spin-up time for warming-up. The output results were time-dependent. Appreciate for the chance to clarify.

28. L.263: P(NOz) should also include the production rates of organic nitrates which can be calculated using the box model results. Depending the fraction of organic production rate in the total NOx consumption rate, the OPE could be significantly over-estimated.

Response: Thanks for your suggestions. This is really an important one and we are sorry our previous calculation missed the organic production rate, such as organic nitrate. In this new manuscript, we include both inorganic and organic production rate.

29. L.272: include units for the measurement results in Heshan. Are the errors standard deviations?

Response: Thanks for the advice. In the latest version we include units for all results. Yes, they are standard deviations.

30. L.279: (O1D).

Response: Thank you for this detail. Modified as suggested.

31. L.281: is 93 ppbV for hourly or 8-hour maximum?

Response: Yes, it is.

32. L. 282-284: How come that VOC concentration in Beijing and Heshan are the same (i.e, Table S3 and Table S4 are identical)? Alkanes made up over 60% of the summed VOCs in Beijing. Is this in terms of concentration or VOC reactivity? Please clarify.

Response: We are so sorry for this careless mistake. We have corrected it in this new version. This percentage is in terms of volume concentration.

33. L.294: photochemical age is mentioned here but it is not defined until next paragraph. It's not presented in Fig. 6-7 either.

Response: Thanks for the advice. However, as we saw in most literatures concerning photochemical age, I found most of them considering the phrase as known to readers and present no special explanation for it. But if it's necessary, we think the equation 3-1 should be enough. Appreciate for your careful suggestion.

34. L.314: Please define LTC.

Response: Thanks for the suggestion. We have modified it to “local time”.

35. L.325: again the two decimals are not significant considering the relatively large uncertainty of 5 s^{-1} *in the measurements. Please correct all reported numbers for OH reactivity.*

Response: Thanks for this. We have modified as you suggested in 1.

36. L.330-331: the morning rush hour peak could be because of a shallow boundary layer.

Response: Thank you for suggestion. Yes, the shallow boundary layer could be an important factors. However, there were two reasons we think primary emissions could be more important or more significant. One is we could find NOx and hydrocarbons connected to vehicle emissions increased faster than other secondary species. The other reason is that the highest peak occurred at 7 o'clock or 8 o'clock, while the boundary layer was not the lowest. However, we admitted the variations of boundary layer really had an important influence on reactivity results.

37. L.335-338: I don't think the little variations in OH reactivity on clean days can fully explain the less variability of OH reactivity in Heshan and in Beijing. It's probably because the air sampled in Heshan is more aged (as the authors have discussed) and regionally mixed than in Beijing.

Response: Thanks for suggestions. The reviewer's suggestion could be one of the reasons and we have included in the revised paper. However, the 2 periods of clean air really caused a significant influence on the diurnal variation average.

38. L.353-354: please give the absolute missing OH reactivity values in s^{-1} *for both location. A comparison between the missing OH reactivity and the combined uncertainty of measured (5* s^{-1}*) and calculated (from the measured species) OH reactivity is needed in order to see if the missing OH reactivity is significant. The uncertainty of measured OH reactivity should be also discussed somewhere in Section 4 when the contribution to the missing reactivity is discussed.*

Response: Thanks for the advice. The absolute missing OH reactivity values have been included in the latest manuscript: over 4 s^{-1} in Beijing and 10 s^{-1} in Heshan. The direct comparison with the average missing reactivity and combined uncertainty of measured and calculated reactivity were weakened because of the difference with time-series. In some time, the measured and calculated reactivity could be close within 5 s^{-1} difference, while in other periods like in Section 4, the difference could be over 30 s^{-1}. For this work, we focus mostly on the periods with significant missing reactivity, as picked in Section 4.

39. L.357: the entire campaign.

Response: Thanks for the advice. Accepted and modified as suggested.

40. L.363-364: "the relative reactivity compared to NMHCs mixing ratios were higher."

Response: Thanks for the suggestion. Accepted and modified.

41. L.399: the sentence, "We found only one datasets in 2005 measured by NOAA (Liu et al, 2009)." is not clear to me. One dataset of what?

Response: Thanks for asking and sorry for the misunderstanding. It should be the dataset of branch-alkenes measurements.

42. L.400-402 and Fig.11 lower panel: missing OH reactivity is plotted against the reactivity assumed from 4 branched alkenes. What are these 4 alkenes; are they representative for the missing alkenes; and how is the calculation performed? Please clarify.

Response: Thanks for asking. The four branched alkenes were iso-butene, 2-methyl-1-butene, 3-methyl-1-butene and 2-methy-2-butene. For the calculation, we have two datasets, one is the missing OH reactivity diurnal variation in 2013, and the other is the branched-alkenes measured in 2005. We tried to correlate the missing OH reactivity and branched-alkenes reactivity, as shown in Fig 11.

43. L.402-403: consider to change this to: "even with the mixing ratios of the 4 branched alkenes measured in Beijing in 2005, the reactivity…"

Response: Thanks for advice. Accepted and modified as suggested. It is much easier to understand.

44. L.419-420: need a reference for the statement that the mixing ratios of branched alkenes could be lower than 0.1 ppbV. The site in Beijing is only a few hundred meters from major roads and can easily get influenced by vehicle emissions.

Response: Thanks for asking. This was from the later measurements in 2015, which has not been published yet. Also we could achieve similar results if we used the emission ratio method. If we assume the emission ratio of branched-alkenes to chained-alkenes remains constant between 2005 and 2013, we could get the calculated mixing ratios of branched-alkenes, which were lower than 0.1 ppbV.

45. L.425-426 and Table S5: not sure if I understand the "major secondary contributors to modeled reactivity." Why only these species are listed in Table S5? Are they related unmeasured intermediates that are calculated in the model? Need definitions for the acronyms in the model (ALD, DCB, etc.).

Response: Thanks for the questions. These five categories contributed the most among the secondary species modelled in the box model. And thanks for the advice about the explanation for the acronyms, the supplementary files has been revised to include the information.

46. L. 460-462: It's not clear to me how the remaining missing reactivity were allocated into different intermediates. Are these intermediates constrained (remained constant) in the box model run in the second scenario?

Response: Thanks for asking. These intermediates were not constrained in the box model run for the OPE calculation. We just allocate the missing reactivity into these intermediates. As you can see, there could still be missing reactivity between modeled reactivity and measured reactivity. So for the OPE calculation, we are not using the modeled reactivity we've got in 4.3, but just allocate the missing reactivity to different intermediates. However, this will be an important uncertainty for our evaluation.

47. L.466: on average. Also please give absolute values, i.e., increase from XX to YY.

Response: Thanks for the detail. Accepted, and due to the variations of OPE with NO_2, we decided to choose 20 ppbV as one example.

48. Section 4.4: again, the OPE needs to be recalculated by including the production rate of organic nitrates in P(NOz). This may change the picture currently shown in Fig.14.

Response: Thanks for advice. Accepted and modified as suggested.

49. L. 497-499: Need to include the modeled OH reactivity in Fig. 11. Without this, it is hard to assess this statement that missing OH reactivity can be reconciled with modeled intermediates that were not measured. Also this statement seems in contrast with the statement in L. 395-399, where the author stated that unmeasured primary VOCs, especially branched alkenes, are responsible for the missing OH reactivity. Please clarify.

Response: Thanks for suggestion and question. For the Fig.11, we have modified as suggested. For the question, I think it was a problem caused by my inappropriate expression. In L.395-399, we are considering the important contribution from unmeasured primary VOCs, especially the branched-alkenes in morning rush hour. However, in L.497-499, we are summarizing the daytime modeling work. The August 17th morning was an exception for the evaluating, which left a great missing percentage unsolved.

50. L. 507-510: probably add a sentence stating that efforts to reduce the uncertainty *of OH reactivity measurements based on the CRM technique to increase the confidence of results as shown in this work.*

Response: Thanks for your suggestions. Accepted and modified.

51. Fig.5: please give the Grade II of National Ambient Air Quality Standard for ozone and PM2.5 in the caption. Also it seems the two red lines in Fig. 5-a and Fig. 5-b are different, one above 80 ppbV and the other below 80 ppbV. Please clarify.

Response: Sorry for this mistake. We have modified the figures as you suggested.

52. Fig.6: the yellow (or brown) lines show the NO fraction (not percentage) in NOx. Please correct it.

Response: Thanks for this advice. This is due to my misunderstanding.

53. Fig.11: please plot the modeled OH reactivity, the same as in Fig. 12. Is the gray area along the red line showing the uncertainty of the measurement? If so, please state this in the caption.

Response: Thanks for suggestions. Figures revised and the explanation added.

54. Fig.14: references for OPEs in other studies should be given.

Response: Thanks for advice. Accepted and modified as suggested.

55. Again, Table S5 and Table S6 are identical.

Response: Sorry for this careless mistake. Modified as in the new supplement.

56. P. 3 of the supplement: in Alkenes, ethane should be ethane.

Response: Thanks for advice and sorry for this mistake.