Reply to Reviewer's comments

General Comments

The paper by Yang et al. report 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 calculated the ozone production efficiency (defined as ratio of ozone production rate/NOx 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 NOx concentration environments. Such a study would certainly be of great interest to the ACP leadership 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 datasets and conclusions. The presentation and language also needs to be improved before it can be considered suitable for publication in ACP.

Response: Appreciate your comments. As you have said above, there're a lot of problems in our previous manuscript, whether in technical part or language part. Wish these answers and latest version of the paper could help with it.

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 from 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 pyrr/OH ratio, would ensure better accuracy and take into account correction factors for each type of standard.

Response: Thanks for asking. This is a mistake and in the latest version of manuscript, we have included some fundamental parameters of the CRM system. In the last paragraph of 2.1.1, we re-phrase it as below:

Ambient air or synthetic air was introduced at 160 -170 ml min^{-1} with the total flow 320 – 350 ml min^{-1}(The typical dilution factor was about 2-2.15 depending on the situation). The residence time of air inside the reactor was less than 30 s before they were pumped by the Teflon pump. The typical c1 mixing ratio for pyrrole in Beijing and Heshan measurements were about 60 ppbV and 55 ppbV, while the mixing ratios of OH radicals generated by mercury lamp were about 35 ppbV and 28 ppbV. The mixing ratios were quite consistent for either of the campaigns, respectively.

Also we have tried the FACSIMILE model for the deviation to achieve the equations 2-2 and 2-3.

Also your suggestion may be right, the pyrrole/OH ratios from propene and propane were different due to the slightly different ratios used in two periods of time. This would introduce uncertainty in our measurements.

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 concentrations 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 NOx-VOC chemistry for OH formation. Instead corrections are valid only for NO concentrations inside the reactor.

I am also puzzled that the concentration factor (delta s-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 deployment (>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 and propene or a mixture of few compounds cannot yield robust corrections 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 more 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 5a and 5b, 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 issure 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 5a and 5b for an idea of temporal variations in both the measured OH reactivity and calculated OH reactivity. At present only few days of time series data from both sites have been presented in Fig 11 and Fig12.*

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 (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 experiments better in high NOx environments can be an outcome of the present study.

Response: Thanks for the advice. This is the key question to the CRM technique in this work. For the first question, the NO concentrations we used in the calculation were “ambient” NO concentrations, which were introduced into the system with synthetic air. We assumed this was the starting situation for the reaction and calculation. We did not have the NO measurements in the CRM reactor and could not quantify the concentrations well, thus we could not calculate the coefficients for the equations.

The second question remains unsolved even to us. We would expect the same situation as the referee did. The difference in quantities of reactants should have a different influence on the NO recycling and thus a different delta reactivity. However, after we’ve tried the experiments several times with different standard gases, we’ve found the correction curve were very close. We are still pursuing the principles underlying but we’ve not reached a persuasive one.

For the method, most of the colleagues suggest that we should deploy the advantages of flow adjustment. However, that advantage is very useful when the observation site is changed or the forecasts predict the coming of a heavy polluted air masses. However, like in Peking University Site, which was close to vehicular emissions, high levels of NO always come in several minutes and not enough time is left to flow adjustment and system stabilization. If we set the ratio of nitrogen to ambient air too high, maybe the OH reactivity of diluted samples will be too low to reach detection limits. But with our experiments, we believe in our corrections and employ the correction curve to obtain the measured reactivity. And for these two observations, the corrections in the manuscript presented the best we can do at that time.

For the relationship between measured reactivity and NO, we found similar diurnal patterns between measured reactivity and NO_x, which were dominated by NO_2 in both sites. For the comparison between measured and calculated reactivity, we would like to focus on the missing reactivity in some pollution episodes. However, if the referee insists, we could supply with the similar figures as Fig 5a and Fig 5b with calculated reactivity included.

Thank you very much for these three paragraphs discussion.NO interference is really the most important and annoying problem concerning CRM technique. For further researches, more effort will be put in the experimental and analyzing work. For experimental part, the experiments should be undertaken more carefully and systematically to figure out the key factors influencing the NO interference. For analytic part, we need to find one way to find the correction curve and explain it in a principle way.

3) NO_2 measurements and ozone production efficiency calculation in model using calculation NO_2: The authors mention (Lines 221-223; page 8) that the NO_x measurements were performed using the chemi-luminescence 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 NO_2 instruments have been shown to overestimate the NO_2 concentration by up to 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. Rudzin Ski (eds,), DOI 10.1007/978-94-007-5034-0_2, # Springer Science + Business Media Dordrecht 2013. The authors mention that they used that measured NO_2 to constrain the model (lines 246-248; page 9). If the measured NO_2 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 $P(NO_z)$ (Equation 2-3). This could affect their conclusions majorly and the authors should address their concern.

Response: Thanks for the advice. This recent piece of literature really brings a big question about the reliability of NO_2 measurements. Especially in our calculation and analysis, the contribution from NO_2 to total OH reactivity is very large. However, we could only supply with one piece of supportive evidence for our manuscript. In Heshan, we have two set of NO_x analyzers. One was equipped with a home-build photolytic converter (NO_x-PL) and the other one was equipped with a catalytic converter (NO_x-Mo), both were similar as the setups of the instruments in Tan et al (2017). This comparison could help us to figure how great the interference could NO_z have on the measurements. From the data comparison, we found that the datasets were close within 10% for most of the time but could be over 20% when in some nights or morning time. However, we have no similar inter-comparison in Beijing measurements. However, this could be a great interference and should call our attentions in later research.

Other Comments:
Abstract:
(Line 22; Page1) and elsewhere in the paper: The authors should report the measured OH reactivities and other concentration measurements by rounding off to significant figures.

Response: Thanks for the advice. Modified as suggested.

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

Response: Sorry for this mistake and revised as suggested.

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

Response: Thanks for the advice and changed as suggested.

Line 46, Page2: should be "reactive" instead of "reductive"

Response: Thanks for asking. However, we think the species here are the species could react with OH radicals, which should be reductive species. Appreciate your suggestion anyway for this clarification.

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

Response: Thanks for the advice about this latest results and included in Table 2 in last manuscript.

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.

Response: Thanks for advice. Modified as suggested.

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?

Response: Thanks for these details. The last sentence of this paragraph was modified as below: Ambient air was sampled after a teflon filter and then pumped through a 14.9m Teflon 3/8 inch (outer diameter) inlet at about 7 L·min-1 rate, with a 5 - 6 s residence time.

Line 159-164; Page 6: Humidity adjustments to synthetic air for matching ambient humidity changes: It is difficult to imagine how the simple need valve contraption 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.

Response: Thanks for asking. This is really an important part for the work. The needle valve we used in the experiments could not adjust itself to certain humidity. However, once we set it to certain position and it could remain the relative humidity for quite a long time. However, as it was tuned manually rather than automatically, it could not track the ambient humidity and could only be adjusted by the operator when he was free to check the humidity and adjust it. That was also why the correction equation was needed for further corrections. The figure for one example is supplied in latest version of supplement information.

Line 167; Page6: Spelling error: "generated"

Response: Thanks for the careful check and modified as suggested.

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.

Response: Thanks for asking. First, HONO results ranged from several tens of pptV to several ppbV in Heshan campaign. However, the data was under-preparation for publications now so I did not present the figures in this paper. Second, while the HONO was just 100 pptV or so, the influence was not very significant. However when the ambient HONO mixing ratio was over 5 ppbV, which was observed in the campaign, the influence should not be omitted. Moreover, the HONO peak came out several times with low reactivity periods, which called for more careful corrections.

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

Response: Thanks for suggestions and modified.

In the supplement Table S3 and S4 are identical except for the captions!
In the supplement Tables S5 and S6 are identical except for the captions!

Response: Thanks for the check and very sorry for this careless mistake. Modified in the new manuscript.

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 assumptions of approximating P(NOz) as P(HNO3)

Response: Thanks for this question very much. Referee 3 also brought this question, which was a big problem in previous calculation. In the new version, we include the organic nitrate part in the calculation and the results could be a little different.

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?

Response: Thanks for asking. We've checked the data. There're some points too low which we think the data was influenced by the zero-calibration. However, for most of the data, we think they're valid. I think some of the points appeared very low in the figure due to the large axis. When the CO mixing ratio was about 100 ppbV, you could not find the point in the figure. However, the suggestion is important for us.

Section 3.1: Figure 5-a: There seems to negative mass concentration of PM2.5 on 17, 19, 23, 25 and 26 October evening which are masked because the axis starts from zero. Please explain.

Response: Thanks for asking. We're using the TEOM for PM2.5 measurements, and our instrument could not measure precisely when the PM2.5 concentration was very low. So there're some points below zero but that makes no sense so we delete the data below zero and then we got the figure as you saw.

Figures 6: I cannot make our much as the 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.

Response: Thanks for the question. The figures were modified in the latest version of manuscript. NO/NOx ratio was lower in Heshan compared to Beijing, and the other factor was the time when NO went down to near zero. With these two factors, and also other explanation listed after this paragraph, we assume that Heshan is influenced by transported air masses compared to Beijing.

L317 and 319: The unit of OH concentration should be molecules cm-3 (and not moel cm-3). Similarly in L314 and 316, mole should be replaced by molecules.

Response: Thanks for the advice and revised as suggested.

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

Response: Thanks for the suggestion and modified in the figures.

Figure 8: Use appropriate legends? Not clear what is meant by "reac_mea_median"

Response: Thanks for the suggestion and modified as k_{mea}_median and explained as the median results of measured reactivity.

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

Response: Thanks for mentioning that. This was correct but we select the two episodes for the accumulation of secondary pollutants.

L348-352: Reasoning is not clear: This contradicts the previous statement that Heshan receives more aged air masses. Aged air masses should also show more contribution from OVOCs. Moreover if faster photochemical 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.

Response: Thanks for the question. I think the expression in previous manuscript was not good. So we re-phrase it with no expression comparing the OVOC percentages in both sites. Your suggestion is right that the measuring seasons were different in both sites which would significantly influence the secondary species production rate. However, there was another possibilities lying in the missing reactivity. However, the previous expression was inappropriate. Appreciate the advice.

L425: 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.

Response: Thanks for the advice. In the latest version, we explained the species concerning these four categories. For the HCHO part, we've included HCHO as an input for the model, so the k_{cal} and k_{mod} was almost the same and thus we did not present the k_{cal} in the table. However, appreciate the question.

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 NOx consumed.*

Response: Thanks for the suggestions and modified as advised.

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.

Response: Thanks for asking. I am not sure about the logical question here. We have mentioned two probable explanations in 4.2 and 4.3 and then take them into consideration in 4.4 to calculate the OPE here. If we exclude these alkenes and OVOCs, then the calculation would appear un-constrained. However, I am not sure whether we should take other species into consideration.

The LOD reported for the CO, NOx and O_3 *instruments in the supplement are much less than what is claimed by the instrument manufacturers in their manuals (40 ppt for NOx, 1 ppb for* O_3*, and 40 ppb 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.*

Response: Thanks for asking. However, after checking with our engineers, these were typical running conditions for these instruments for several campaigns since CAREBEIJING-2006 and PRIDE-PRD2006 (Lu et al 2012; 2013).

Reply to Reviewer's comments

General Comments

The manuscript presents OH reactivity measurements from two urban sites in China and compared the OH reactivity data to calculated and modelled reactivity determined from the individually measured, co-observed OH sinks. Ozone production efficiency (OPE) is calculated from measured and modelled reactivity and the authors conclude that missing OH reactivity can increase ozone production efficiency at both sites. Understanding total OH reactivity by considering the dominant species contributing to OH reactivity and identifying missing OH reactivity and how this influence ozone production in urban environments is important and a suitable subject for ACP. The conclusion that more aged air-masses have a higher % of missing reactivity is an important finding also. Unfortunately there are several major problems with the manuscript currently which mean that the results and interpretation of the results are over-shadowed: The technical concerns (already thoroughly covered by Reviewer 1) relating to the quality of the OH reactivity data from the CRM instrument under high NO_x *conditions where large corrections have been applied need to be addressed before final publication. Furthermore, a more comprehensive comparison between the observed reactivity and calculated and modelled reactivity should be included and discussed to strengthen the overall conclusions drawn. I struggled to evaluate much of the discussion and conclusions, largely due to the poor English, but also because data discussed in the text did not appear in the referred figures or table: the modelled reactivity is not included in Fig. 11 upper panel and the breakdown of modelled reactivity is duplicated in tables S5 and S6. The figure axes and figure and table captions are inadequate to understand the data presented and there are inconsistencies between the data presented in the figures and discussion provided in the text. I have made a number of recommendations below where further clarification is needed or where the discussion should be improved before final publication can be considered.*

Response: Appreciate the general comments on this manuscript. We accept the comments on poor English and modified to this version. Wish this time it's easier to understand.

Line 30: '… by adding unmeasured oxygenated…' this suggests that the model was constrained to assumed concentrations of OVOCs, but I don't think this was the case so this sentence needs revising

Response: Thanks for asking. We are constraining the box model with several measured carbonyls, such as acetaldehyde, acetone.

Line 34: change '.. such as aldehydes..' to '.. such as unmeasured aldehydes..'

Response: Appreciate the suggestions and accepted.

Model description: Line 230: How were the VOC data inputted into the model given the 1 hour time resolution of these measurements and 5 min time resolution of the model?

Response: Thanks for asking. For VOCs data, we were using the linear interpolation method to achieve the 5 min time resolution and then put the data into model.

In section 4 the authors consider the contribution unmeasured primary and secondary VOCs may make to missing reactivity. To strengthen this discussion some commentary is needed on the sensitivity of modelled OH reactivity to some of the assumed model parameters: Line 251: Are there local sources, e. g. roads, which mean that unconstrained products are not in steady state? How different is modelled reactivity on day 1 vs day 3 spin up? Line 251-253: How sensitivity is modelled OH reactivity to the treatment of dry deposition in both locations? How was the changing boundary layer height treated in the model? Could this influence the diurnal profile of the modelled OH reactivity?

Response: Thanks for asking. Firstly, we admit that the model we were using in this manuscript was really a simple one. The close primary emissions, surly would introduce large uncertainty on the model job. However, as we were using this observation-based model, we could not input the emission data. The way we dealt with this problem was trying to do the moving average to avoid the sudden increase of decrease of certain species. For different spin-up time test, we found modelled OH reactivity could be different within 10% between two situations. However, for the literature suggestion and the 24 hour deposition time we chose, we decided to choose 3 day spin-up. For the dry deposition, some OVOCs and secondary species were quite sensitive to the dry deposition choice. From literature (Lu et al, 2012; 2013), we chose 24 hour dry deposition, and the modelled OVOCs presented similar diurnal variations of observations, with a 15%-30% difference depending on species. For the boundary layer height, we determined to set a well-mixed boundary layer height of about 1 km. However, this could be a source of uncertainty due to the diurnal variation of boundary layer height. Moreover, from Lu et al (2013) and Tan et al (2016), we would know that there could be missing chemistry in the nocturnal boundary layers, which would introduce unconstraint species and reactions in model work. However, due to the lack in boundary layer height measurements, we decided to set a constant boundary layer height. But the advice above are all important and appreciate all the questions.

Results: Line 317 and 319: Are these the peak OH concentrations at both sites? Given the photochemical age of the air masses wouldn't a mean OH concentration be most appropriate for this calculations? The authors should discuss briefly the sensitivity of the photochemical age to [OH] used.

Response: Thank you very much for this suggestion. These are both the peak OH concentrations in diurnal variations. Yes, this is one mistake and for the mean OH concentrations should be the most appropriate. Also in the latest manuscript, we include a short sentence concerning the influence from OH concentration on photochemical age calculation. Appreciate your help.

Line 348: Please provide details on the data used to generate the pie-charts – is this the campaign average picture? How does this change in Heshan during the pollution episodes? It would be informative to include a time series of calculated OH reactivity, modelled OH reactivity and measured OH for the whole of the two campaign periods somewhere in the manuscript.

Response: Thanks for asking. It is the campaign average. However, it only included the data when there were OH reactivity measurement results. The data used to generate the pie-charts were as follows. However, we thought with this pie-charts, we did not need to present the data as well. For the second question, we could include the figure the referee asked for Heshan campaign. However, in Beijing observation, due to the discontinuity for OH reactivity and VOCs measurements through these three weeks, the modeled reactivity would need many times of interpolation and would thus introduce a great uncertainty here. So we decide to focus on certain processes rather than the campaign average.

L459: '..more significant role..' give % contributions.

Response: Thanks for asking. In latest version of manuscript, we rephrase this sentence as below: The OVOCs had also significant contribution, and measured OVOCs had a sharing of 10% in total reactivity in Beijing while 7% in Heshan. We think the comparison was influenced by many factors, so we give up this direct comparison. Appreciate for this question.

L456-457: What was the level of the NO correction applied to the measurement data during morning rush-hour?

Response: Thanks for asking. This is one important question. For some periods in morning rush hour, when NO mixing ratio over 20 ppbV was observed, the NO correction could be over 40 s-1 for measured reactivity. While the absolute reactivity was about the same level. However, this correction was checked for different species and verified. So we think this results were valid.

Discussion: L363: what is meant by relative reactivity?

Response: The relative reactivity means here the ratio between VOCs reactivity and NMHCs mixing ratios. It's not a strict definition here. However, we did not bring out this phrase at first in the latest version of manuscript. Appreciate your question.

Line 366: '..not very high..' apart from Paris, Heshan VOC reactivity is highest. This *section needs to be revised to accurately reflect the data in Fig. 10.*

Response: Thanks for asking. We re-phrase this paragraph as below: The measured VOCs reactivity (obtained by subtracting inorganic reactivity from total OH reactivity), 11.2s-1 in Beijing and 18.3s-1 in Heshan (Fig 10), was actually not at high end comparing with the levels from literatures. Tokyo presented a similar level of VOCs reactivity (Yoshino et al., 2006) and Paris had an even higher level of VOCs reactivity which was obtained in wintertime (Dolgorouky et al., 2012). The measured NMHCs levels (obtained by adding all hydrocarbon mixing ratios together) were also not very high, with Beijing 2013 being around 20 ppbV and Heshan 2014 higher than 35 ppbV. The relative VOCs reactivity, defined by the ratio of the VOCs reactivity to the measured NMHCs levels, the values for both Beijing and Heshan were very high.

Figure 10a: Why not change the x axis to calculated NMHC reactivity (s^{-1}) *? This would then help to demonstrate the cause for this trend, i. e. a) that the type of measured NMHCs in Beijing are indeed more reactive with respect to OH than at other sites or b) missing reactivity is more significant n Beijing and Heshan vs other sites. The discussion provided in 4.1 should be revised once the figure is changed.*

Response: Thanks for asking. Your suggestion is quite good to clarify the importance of the missing reactivity. However, if we are using the calculated NMHCs reactivity as x axis, we would not know that the first part you’re telling, that the difference in the known compositions. Because we would only know that NMHCs reactivity in Beijing and Heshan were quite high. However, what we would like to express as well is while the NMHCs mixing ratios were not very high in Beijing and Heshan, the NMHCs reactivity could be high in both places. However, in our figure, there remains the questions that how could we presented both problems in one figure.

Figure 10b: They y axis label is missing. Also why is Paris not included in this plot?

Response: Thanks for the suggestion. Accepted and revised.

Line 400: It is unclear whether the NOAA 2005 dataset is from Beijing. Even it is, it doesn’t seem reasonable to simply compare missing reactivity from 2013 with branched alkenes data from 2005. Could a common species, measured both in 2005 and 2013, which is strongly correlated to the branch alkene data be used to scale the 2013 branched alkene data? Why are there only 6pts in figure 11, lower panel?

Response: Thanks for asking. Yes for sure, the NOAA 2005 dataset was from Beijing. For the calculation in this part, we were firstly trying to track the correlation between the branched-alkenes and missing reactivity. So we compare the results in both diurnal variations. However, as we said in the paper. Even the mixing ratios in 2005 was not enough to explain all the missing reactivity, not even to say the decreasing trends for VOCs species in Beijing since 2005. The reason we only got 6 points were mainly due to we would compare the data between morning rush hours in the diurnal variations. Appreciate for the questions to clarify this part.

Figure 11 upper panel: modelled reactivity needs to be added to this plot

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

Lines 424-426: Key to ozone control strategies, the authors should discuss the primary species from which the modelled species derive.

Response: Thanks for asking. Sorry for this paper, the research focuses mostly on whether the primary or secondary species contributed more for the missing reactivity. However, we also have the data to answer your questions. These species were formed mostly as the oxidation products of alkenes and aromatics. However, your suggestion is very important and key to our next step – ozone control strategies. The vehicular emissions and solvent use related to alkenes and aromatics in urban areas should be controlled strictly for ozone reduction.

Table S5: Species names should be provided in full – what is 'DCB'?

Response: Thanks for advice. This is also the advice from other reviewers. We will give a full explanation of major species in the tables.

Lines 444-445: the authors should also compare the calculated and modelled reactivity from 2006 and 2014 too, so the 50% higher measured reactivity in 2014 can be evaluated fully.

Response: Thanks for the advice. However, VOCs measurements from 2006 was limited to offline canister samples and the species were fewer than 2014. We're afraid this compare may be not comprehensive.

Lines 452,453: 'PAMS 56 hydrocarbons' and 'TO-15 OVOCs' needs defining

Response: Accepted. We made an introduction to these two sets of standard gases, but due to the limitation of length, we would not supply the details of these species here.

Lines 465-466; in section 4.3 the authors report that the OH reactivity modelled in Beijing agreed with the measured reactivity in the daytime (lines 423-424), but on lines 465-466 report difference between measured and modelled reactivity in Beijing which changed OPE by 27%. These two statements are inconsistent with each other and as the modelled reactivity is missing from Figure 11 it is unclear which is correct.

Response: Thanks for asking. This is an interesting question. We've got similar questions at first. However, after we double-checked, the results remained the same (though after we take organic nitrate into consideration, the difference was 21%). I think the difference could result from reasons below: 1) though many of the daytime reactivity were the same for the episodes, still some points the measured and modelled reactivity were different, not even to say the significant difference in rush hours; 2) the difference in species composition in scenario 1 and 2. Different species would introduce different levels of ozone production efficiency. However, this remains a question we need to dig in. Appreciate the question.

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 1 σ. 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% (1 σ).

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.

How does the OH reactivity affect the ozone production efficiency: case studies in Beijing and Heshan, China

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Abstract

Total OH reactivity measurements were conducted on the Peking University campus, Beijing in August 2013 and in Heshan, Guangdong Province from October to November 2014. The daily median OH reactivity were 20 ± 11 s^{-1} in Beijing and 31 ± 20 s^{-1} in Heshan respectively. The data in Beijing showed a distinct diurnal pattern with the maxima over 27 s^{-1} in early morning and minima below 16 s^{-1} in the afternoon. The diurnal pattern in Heshan was not as evident as in Beijing. Missing reactivity, defined as the difference between measured and calculated OH reactivity, was observed at both sites, with 21% missing in Beijing and 32% missing in Heshan. Unmeasured primary species, such as branched-alkenes could contribute to missing reactivity in Beijing, especially in morning rush hours. An observation-based model with the RACM-2 (Regional Atmospheric Chemical Mechanism version 2) was used to understand the daytime missing reactivity in Beijing by adding unmeasured oxygenated volatile organic compounds and simulated intermediates of the degradation from primary VOCs. However, the model could not find the convincing

explanation for the missing in Heshan, where the ambient air was found to be more aged, and the missing reactivity was presumably attributed to oxidized species, such as unmeasured aldehydes, acids and di-carbonyls. The ozone production efficiency was 21% higher in Beijing and 30% higher in Heshan when the model was constrained by the measured reactivity, compared to the calculations with measured and modeled species included, indicating the importance of quantifying the OH reactivity for better understanding ozone chemistry.

1. Introduction

Studies on total OH reactivity in the atmosphere have been of increasing interest over the last two decades. The instantaneous total OH reactivity, is defined as

$$\mathrm{k}_{OH} = \sum_i k_{OH+X_i}[\mathrm{X}_i] \qquad (1\text{-}1)$$

where X represents a reactive species (CO, NO_2 etc.) and k_{OH+X_i} is the rate coefficient for the reaction between X and OH radicals. Total OH reactivity is an index for evaluating the amounts of reductive pollutants in terms of ambient OH loss and hence their roles in atmospheric oxidation (Williams, 2008; Williams and Brune, 2015; Yang et al., 2016). It also provides a constraint for OH budget calculation in both field campaigns and laboratory studies (Stone et al., 2012; Fuchs et al., 2013).

Total OH reactivity measuring techniques, e.g., two laser-induced-fluorescence (LIF) based techniques (Calpini, et al., 1999; Kovacs and Brune, 2001) and one proton-transfer-reaction mass spectrometry (PTR-MS) based technique, comparative reactivity method (CRM) (Sinha et al., 2008) were developed in recent years. A brief comparison of these techniques and their interferences were summarized (Yang et al., 2016). By deploying these measuring techniques, total OH reactivity measurements have been intensively conducted in urban and suburban areas. Details of these campaigns were listed in Table 1 and Table 2. Most of the campaigns exhibited similar diel features with higher reactivity in dawn and rush hours of early morning, and lower levels in the afternoon, which could be explained by the change in boundary layer height, emissions and oxidation processes. Anthropogenic volatile organic compounds (VOCs) and inorganics, such as CO and NO_x (NO + NO_2) are major known OH sinks in urban areas.

However, a substantial difference between measured and calculated or modelled OH reactivity, termed as the missing reactivity, was revealed in most field campaigns. Compared to the high percentages of missing reactivity in forested areas (Sinha et al., 2010; Nölscher et al., 2012; 2016; Edwards et al., 2013, Williams et al., 2016), most campaigns in urban and suburban areas gave relatively lower percentages of missing reactivity except for the 75% missing reactivity in Paris in MEGAPOLI under the influences of continental air masses (Dolgorouky et al, 2012).

Various methods were used in exploring the origins of missing reactivity. Unmeasured primary species are important candidates. Sheehy et al. (2010) discovered a higher percentage of missing reactivity in morning rush hours and found that the unmeasured primary species, including organics with semi and low-volatility, could contribute up to 10% of total reactivity. Direct measurements on reactivity of anthropogenic emission sources were conducted, such as vehicle exhaust and gasoline evaporation. An average of 17.5% missing reactivity was found in vehicle exhaust measurements (Nakashima et al., 2010). For gasoline evaporation, a study showed that if primary emitted branched-chained alkenes were considered, the measured and calculated reactivity then agreed (Wu et al., 2015). Besides primary emitted species, unknown secondary species were not negligible. Yoshino et al. (2006) found a good correlation between missing reactivity and measured oxygenated VOCs (OVOCs) in three seasons except for winter, assuming that the unmeasured OVOCs could be major contributors of missing reactivity, in one case the OVOCs could increase reactivity by over 50% (Lou et al., 2010). The observation-based model (OBM) was widely used to evaluate the measured reactivity (Lee et al., 2010; Lou et al., 2010; Whalley et al., 2016), confirming the important contribution from OVOCs and undetected intermediate compounds,.

Ground-level ozone pollution has been of increasing concerns in China. While the ozone concentration exceeds Grade II of China National Ambient Air Quality

Standards (2012) (93 ppbV) frequently in summer in Beijing-Tianjin-Hebei area and Pearl River Delta (PRD) region (Wang et al., 2006; Zhang et al., 2008), it appears there is an increasing trend for ozone in Beijing and other area recent years (Zhao et al., 2009; Zhang et al., 2014). Comparing to traditional empirical kinetic model approach (EKMA) (Dodge et al., 1977), the OH reactivity due to VOCs (termed as VOCs reactivity) rather than VOCs mixing ratio was used in the calculation of ozone production rate (Geddes et al., 2009; LaFranchi et al., 2011; Sinha et al, 2012; Zhang et al., 2014). 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. By directly measuring the total OH reactivity, VOCs reactivity can be obtained by deducting the inorganic reactivity from the total OH reactivity, which provides a constrain for evaluating the roles of reactive VOCs in air chemistry (Sadanaga et al, 2005; Sinha et al, 2012; Yang et al., 2016).

This paper presents field data in China from two intensive observation conducted in August 2013 in Beijing, and October to November 2014 in Heshan, Guangdong, focusing on OH reactivity and related species. The variations of total OH reactivity at both sites were compared with similar observations in urban and suburban areas worldwide. Thereafter, a zero dimensional box model based on Regional Atmospheric Chemical Mechanism 2 (RACM2) was employed for OH reactivity simulations. The possible missing reactivity and its importance for the ozone production calculation are discussed.

2. Methods

2.1 Total OH reactivity measurements

2.1.1 Measurement principles

Total OH reactivity was measured by the comparative reactivity method (CRM) first developed at Max Planck Institute for Chemistry (Sinha et al., 2008). The CRM system was built accordingly in Peking University, it consisted of 3 major components: inlet and calibration system, reactor, and measuring system as shown in

Fig 1. Ambient air was sampled after a teflon filter and then pumped through a 14.9m Teflon 3/8 inch (outer diameter) inlet at about 7 L·min^{-1} rate, with a 5 - 6 s residence time.

In this method, pyrrole (C_4H_5N) was used as the reference substance and was quantified by a quadrupole PTR-MS (Ionicon Analytic, Austria). There are 4 working modes for measuring procedure: In the C0 mode, pyrrole (Air Liquid Ltd, U.S.) is introduced into the reactor with dry synthetic air (99.99%, Chengweixin Gas Ltd, China). A mercury lamp (185nm, used for OH radicals generation) is turned off and high-pure dry nitrogen (99.99%, Chengweixin Gas Ltd, China), is mixed into the reactor through a second arm. In this mode, the highest signals of m/z 68 (protonated mass of pyrrole) c0 are obtained. Then in the C1 mode, the nitrogen and synthetic air is still dry but the mercury lamp is turned on. The mixing ratio of pyrrole decreased to c1. The difference between c0 and c1 is mainly due to the photolysis of pyrrole (Sinha et al., 2008). C2 mode is the “zero air” mode in which synthetic air and nitrogen are humidified before being introduced into the reactor. The photolysis of water vapor generates OH radicals which react with pyrrole in the reactor to c2 level. Then C3 mode is the measuring mode in which the automatic valve switches from synthetic air to ambient air. The ambient air is pumped into the reactor to react with OH radicals, competing with pyrrole molecules. The mixing ratio of pyrrole is detected as c3. Total OH reactivity is calculated as below, based on equations from Sinha et al. (2008):

$$\mathrm{k}_{OH} = c1 \times k_{Pyr+OH} \times \frac{c3-c2}{c1-c3} \qquad (2\text{-}1)$$

Ambient air or synthetic air was introduced at 160 -170 ml min^{-1} with the total flow 320 – 350 ml min^{-1}(The typical dilution factor was about 2-2.15 depending on the situation). The residence time of air inside the reactor was less than 30 s before they were pumped by the Teflon pump. The typical c1 mixing ratio for pyrrole in Beijing and Heshan measurements were about 60 ppbV and 55 ppbV, while the mixing ratios of OH radicals generated by mercury lamp were about 35 ppbV and 28 ppbV. The mixing ratios were quite consistent for either of the campaigns, respectively. Corrections about pseudo-first order kinetics were conducted for both measurements, based on the methods in Sinha et al (2008). The typical correction factors could be presented as

$$R_{true} = 0.0008 * (R_{mea})^2 + 0.78 * R_{mea} – 0.042 \quad (2\text{-}2)$$

$$R_{true} = -0.0004 * (R_{mea})^2 + 0.81 * R_{mea} - 0.017 \quad (2\text{-}3)$$

2.1.2 Calibrations and tests

We performed two calibrations for the measurements. First, PTR-MS was calibrated by diluted dry pyrrole standard gas ranging from less than 10 ppbV to over 160 ppbV (presented in Fig S1). Additionally, we conducted an inter-comparison with humidified pyrrole dilution gas. The sensitivity was about 3% to 5% higher than dry calibration, which was considered for later calculation (Sinha et al., 2009). The tests of the CRM system were done by using both the single standard gas, such as CO, propane, propene (Huayuan Gas Ltd, China) and a standard of the mixture of 56 non-methane hydrocarbons (NMHCs) (SpecialGas Ltd, U.S.). The results of the calibrations and tests were presented in Fig 2. Measured and calculated OH reactivity agreed well within the uncertainty for all calibrations.

A key factor influencing the measurement results is the stability of OH radical generator. One major interference could be the difference in relative humidity between C2 mode and C3 mode. During the experiment, we used one single needle valve to control the flow rate of synthetic air going through the bubbler, so that the relative humidity during C2 mode could be adjusted to match humidity during ambient sampling (C3 mode). Meanwhile, the remaining minor difference could be corrected by factors derived from the OH reactivity-humidity correction experiment. The details of the OH-correction experiment and the data were presented in the supporting information (Fig. S1 and S2).

The other interference might be caused by ambient NO, which produces additional OH radicals via recycling of HO_2 radicals (Sinha et al., 2008; Dolgorouky et al., 2012; Michoud et al., 2015). The amount of OH radical through this pathway is hard to be quantified. In the morning rush hours or on polluted cloudy days, NO levels could rise to over 30 ppbV in both Beijing and Heshan, which could then potentially introduce high uncertainties for measurements. The NO-correction experiments were conducted by introducing given amounts of VOCs standard gases into the reactor. When the stable concentrations for c2 were reached, different levels of NO were injected into the reactor and the “measured” reactivity decreased as the NO mixing ratio increased. Then a correction curve was fitted between the differences in reactivity and NO mixing ratios. Several standard gases and different levels of base reactivity (from less than 30s^{-1} to over 180s^{-1}) have been tried and the curve was quite consistent for all tested gases, as shown in Fig 3. The correction derived from the curve was used later to correct ambient measurements according to simultaneous detected NO levels. The correction was necessary when NO mixing ratio was larger than 5 ppbV, which was quite often observed in the morning time as well as cloudy days in Beijing and Heshan. The relative change for reactivity results could be over 100 s^{-1} when NO mixing ratio was about 30 ppbV.

A further potential interference comes from nitrous acid (HONO). The photolysis of HONO in the reactor could generate the same amount of OH radicals and NO molecules, as shown in R1. The additional OH radicals and NO molecules can be both interferences with the reactivity measurements. Similar correction experiments were conducted as the NO correction experiment. HONO were added stepwise in several mixing ratios (1-10 ppbV), generated by a HONO generator (Liu et al., 2016) and thus introduced into the reactor. A curve was fitted between the differences in reactivity and HONO mixing ratios, as presented in Fig 4. The correction associated with this curve was also applied later in the ambient measurements.

$$\mathrm{HONO} \overset{h\gamma}{\rightarrow} \mathrm{OH+NO} \qquad \text{(R1)}$$

To make sure the production of OH radicals was stable during the experiments, C1 mode was measured for 1-2 hour every other day and C2 mode was measured for 20-30 minutes every two hours. With above calibrations and tests into consideration, the detection limits of CRM methods in two campaigns was around 5 s^{-1} (2 σ). The total uncertainty of the method was about 20% (1 σ), due to rate coefficient of pyrrole reactions (15%), flow fluctuation (3%), instrument precision (6% when measured reactivity > 15 s^{-1}), standard gases (5%) and corrections for relative humidity (5%).

2.2 Field measurements

2.2.1 Measuring sites and periods

The urban measurements started from August 10th to August 27th, 2013 at Peking University (PKU) Site (116.18°E, 39.99°N), which was set on the roof of a 6-floor building. The site is about 300 m from the 6-lanes road to the east and 500 m to the 8 -lanes road to the south. This site is an urban site used for intensive field measurements of air quality in Beijing for long. Detailed information about this site can be found elsewhere (Yuan et al., 2012).

Suburban measurements were conducted from October 20th to November 22nd 2014 at Heshan (HS) site, Guangdong (112.93°E, 22.73°N). The site is located on top of a small hill (60 m above ground) in Jiangmen, which is 50km from a medium size city Foshan (with a population of about 7 million) and 80 km from a megacity Guangzhou. This is the super-site for measurements of air quality trends by Guangdong provincial government, detailed information about which can also be found in Fang et al (2016).

2.2.2 Simultaneous measurements

During both intensive campaigns, fundamental meteorological parameters and trace gases were measured simultaneously. Meteorological parameters, such as temperature, relative humidity, pressure, wind speed, wind direction were measured. NO and NO_x mixing ratios were measured by chemi-luminescence (model 42i, Thermo Fischer Inc, U.S.), and O_3 was measured by UV absorption (model 49i, Thermo Fischer Inc, U.S.). CO was measured by Gas Filter Correlation (model 48i, Thermo Fischer Inc, U.S.), and SO_2 was measured by pulsed fluorescence (model 43C, Thermo Fischer Inc, U.S.). The photolysis frequencies were measured by a spectral radiometer (SR) including 8 photolysis parameters. These parameters were all averaged into 1-minute resolution. The performances of these instruments were presented in Table S1 and Table S2.

VOCs were measured by a cryogen-free online GC-MSD/FID system, developed by Peking University (Yuan et al., 2012; Wang et al., 2014a). The time resolution is 1 hour but the sampling time starts from the 5th minute to 10th minute every hour. The system was calibrated by two sets of standard gases: 56 NMHCs including 28 alkanes, 13 alkenes and alkynes, 15 aromatics; EPA TO-15 standards (http://www.epa.gov/ttnamti1/les/ambient/airtox/to-15r.pdf), including additional OVOCs and halocarbons. The detection limits ranged from 10ppt-50ppt, depending on the species. Formaldehyde was measured by the Hantzsch method with time resolution of 1 minute. Detailed information about this instrument is described in one previous paper (Li et al., 2014).

2.3 Model description

2.3.1 Box model

A zero-dimensional box model was applied to produce the unmeasured secondary products and OH reactivity for both field observations. The chemical mechanism employed in the model was RACM2 (Stockwell et al., 1997, Goliff et al., 2013), with implementation of Mainz Isoprene Mechanism (MIM, Pöschl et al., 2000) and update versions by Geiger et al. (2003) and Karl et al. (2006) for isoprene reactions. The model was constrained by measured photolysis frequencies, ancillary meteorology and inorganic gases measurements, as well as VOCs data. Mixing ratios of methane and H_2 were set to be 1.8 ppmV and 550 ppbV. The model was calculated in a time-dependent mode with 5-min time resolution. Each model run started with 3 days spin-up time to reach steady-state conditions for long-lived species. Additional loss by dry deposition was assumed to have a corresponding lifetime of 24 hours to avoid the accumulation of secondary productions.

2.3.2 Ozone production efficiency

Ozone production efficiency (OPE) is defined as the number of molecules of total oxidants produced photochemically when a molecule of NO_x was oxidized (Kleinman, 2002, Chou et al., 2011). It helps to evaluate the impacts of VOCs reactivity on ozone production in various NO_x regimes. In this work, the OPE was expressed as the ratio of ozone production rate (i.e. $P(O_3)$) to NO_x consumption rate (i.e. $D(NO_x)$). NO_z, calculated as the difference between NO_y (sum of all odd-nitrogen compounds) and NO_x, was assumed to be the oxidation products of NOx. Thus the

OPE could be also calculated as $P(O_3)/P(NO_z)$. The ozone production rate is obtained as 2-2, and the $P(NO_z)$ is approximately as production rate of HNO_3 as well as the production rate of organic nitrate, which is given as 2-3.

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum_i k_{RO_{2_i}+NO}[RO_{2_i}][NO] \qquad (2\text{-}2)$$

$$P(NO_z) = k_{NO_2+OH}[NO_2][OH] + \sum_i k_{RO_i+NO_2}[RO_i][NO_2] \qquad (2\text{-}3)$$

3. Results

3.1 Time series of meteorology and trace gases

The time series of selected meteorological parameters and inorganic trace gases were presented in 5 minute averages (Fig 5). The median values of the inorganic trace gases were 0.715 ± 0.335 ppmV for CO, 6.3 ± 5.75 ppbV for NO and 36.5 ± 21.3 ppbV for NO_2, 57 ± 44 ppbV for O_3 in Beijing. In Heshan, the median results were 0.635 ± 0.355 ppmV for CO, 9.7 ± 6.95 ppbV for NO, 29.6 ± 12.6 ppbV for NO_2, and 55.7 ± 34.9 ppbV for O_3. Both results were within the range of data from literatures (Zhang et al., 2008; Zheng et al., 2010; Zhang et al., 2014). However, daytime averaged O_3 mixing ratio in Beijing 2013 was a little lower than the medium results (about 60 ppbV) in normal years (Zhang et al., 2014). This could be due to higher frequencies of cloudy and rainy days, which accounted for about 1/3 of our measurement duration. The measured maximum photolysis rates in cloudy/rainy days were about half of peak values of J (O^1D) on sunny days. Even under this circumstances, ozone levels from the campaign remained high, the pollution episodes with ozone exceeding Grade II of China National Ambient Air Quality Standards (93 ppbV) occurred quite often, and the percentage of exceedance were 40% in Beijing and 20% in Heshan.

The mixing ratios of VOCs in both campaigns were presented in Table S3 and Table S4. In summer Beijing, alkanes accounted for over 60% of the summed VOCs mixing ratios during most of the time, while in Heshan the contribution from aromatics was 6% higher than that in Beijing. This could be explained by stronger emissions from solvent use and paint industry in the PRD region (Zheng et al., 2009). The ratio of toluene to benzene, which is typically used qualitatively as an indicator for aromatics emission sources also supported this assumption. While this ratio in Beijing was close to 2, similar to vehicle emissions (Barletta et al., 2005), the ratio in Heshan was higher than 3 due to strict control of benzene in solvent usage these days (Barletta et al., 2005; Liu et al., 2008). In the ozone polluted episode in Fig 5, the mixing ratios of most species were about twice to three times higher than the daily average results.

The diurnal variations of NO_x, O_3 and photochemical age from Beijing and Heshan site were compared in Fig 6 and Fig 7. Both sites presented similar diurnal patterns for O_3 and NO. However, the highest 1-hour average O_3 value at PKU site came in the afternoon and stayed at high level till the dawn. While O_3 pattern at Heshan site did not stay high in the afternoon. An additional similarity was that the NO peaks occurred at similar times for both sites. But NO decreased at a slower rate in Heshan till even 12:00 p.m. This was likely explained by the facts that the NO observed at PKU site was mainly from local vehicle emissions while NO_x at Heshan site was significantly influenced by long-range transported of air masses.

VOCs measurements provided us chance to evaluate the oxidation state at two sites. Based on the OH exposure calculation methods (de Gouw et al., 2005), we chose a pair of VOCs species: m,p-xylene and ethylbenzene to calculate the photochemical age:

$$[\mathrm{OH}]\Delta \mathrm{t} = [\ln(\frac{[E]}{[X]})_t - \ln(\frac{[E]}{[X]})_0]/(k_E - k_x) \quad (3\text{-}1)$$

Here, [E] and [X] represents the mixing ratios of ethylbenzene and m,p-xylene, k_E and k_X means the OH reaction rate coefficient of ethylbenzene and m,p-xylene. As presented in Fig 7, we chose 1.15 ppbV ppbV^{-1} and 2.3 ppbV ppbV^{-1} as emission ratios of ethylbenzene to m,p-xylene in Beijing and Heshan, as they were the largest ratios in diurnal variations for the campaign. The largest OH exposure in Beijing 2013 was calculated as 0.71×10^{11} molecule s cm^{-3} in 13:00 LTC, while the largest OH exposure in Heshan 2014 was calculated to be 1.69×10^{11} molecule s cm^{-3} in 14:00 LTC. The results in Beijing were comparable to previous reports (Yuan et al., 2012). Assuming the daytime average ambient OH concentration was 5.2×10^6 molecule

cm^{-3} (Lu et al., 2013), the photochemical age in Beijing was estimated to be not more than 3.5 h. With measured daytime average OH concentration as 7.5 × 10^6 molecule cm^{-3} in Heshan (Tan et al., in preparation), the photochemical age in Heshan was about 6 h to 7 h, which was about twice the photochemical age of the Beijing observations, indicating a more aged atmospheric environment in Heshan. However, the assumed OH radical concentrations' influence on the photochemical age results should not be neglected.

3.2 Measured reactivity

Total OH reactivity ranged from less than 10 s^{-1} to over 100 s^{-1} in Beijing (Fig 5a). The daily median value was 20 ± 11 s^{-1}. The diurnal patterns changed significantly from day to day (Fig 8). The averaged diurnal pattern showed that the total OH reactivity was higher from dawn to morning rush hours with a peak hourly mean of 27 s^{-1}, and decreased to a lower value, median value of 17 s^{-1} in the afternoon. This diurnal pattern was similar to the variations of NO_x mixing ratios (Williams et al., 2016).

Meanwhile, measured total OH reactivity in Heshan was higher in median but the diel variation was less evident. The daily median value was 31 ± 20 s^{-1}. The OH reactivity was much less variable in the daily variation. This could possibly due to the more aged air masses in Heshan, as presented in 3.1. The other probable explanation could be the two periods of clean air we encountered, during which ground-level ozone and $PM_{2.5}$ concentrations were rather low, each of the cases lasted for about 5 days during our measurements. And 2 pollution episodes were identified between October 24th to 27th and November 14th to 17th, 2014. Both episodes showed accumulation of ozone and $PM_{2.5}$. The total OH reactivity level also built up significantly (Fig 5b).

3.3 Variations in missing reactivity

Significant differences were found between the measured reactivity and calculated reactivity which derived from mixing ratios of different species multiplied by their rate coefficients with OH radicals. Taking all measured species into consideration, NO_x and NMHCs showed the largest contribution, 45%-55% of total

OH reactivity (Fig 9). The OVOCs had also significant contribution, and measured OVOCs had a sharing of 10% in total reactivity in Beijing while 7% in Heshan.

The Missing reactivity was on average over 4 s^{-1}, 21 ± 17 % of the total OH reactivity in Beijing and 10 s^{-1}, 32 ± 21% in Heshan. The missing reactivity presented different temporal patterns. In Beijing, the missing reactivities were high during pollution episodes, especially in the morning rush hours. The percentage of missing reactivity could reach over 50%. For the Heshan site, the missing reactivity was more or less stable during the entire campaign. Even in clean days with reactivity levels lower than 20 s^{-1}, 20%-30% of missing reactivity still existed.

4. Discussion

4.1 Reactivity levels in Beijing and Heshan

The measured VOCs reactivity (obtained by subtracting inorganic reactivity from total OH reactivity), 11.2 s^{-1} in Beijing and 18.3 s^{-1} in Heshan (Fig 10), was actually not at high end comparing with the levels from literatures. Tokyo presented a similar level of VOCs reactivity (Yoshino et al., 2006) and Paris had an even higher level of VOCs reactivity which was obtained in wintertime (Dolgorouky et al., 2012). The measured NMHCs levels (obtained by adding all hydrocarbon mixing ratios together) were also not very high, with Beijing 2013 being around 20 ppbV and Heshan 2014 higher than 35 ppbV. The relative VOCs reactivity, defined by the ratio of the VOCs reactivity to the measured NMHCs levels, the values for both Beijing and Heshan were very high.

One possible explanation is the higher content of reactive hydrocarbons in China. Compared to other campaigns, both sites had higher loading of alkenes and aromatics (Yuan et al., 2012; Wang et al., 2014b). The other probable reason is the contribution from OVOCs. In Beijing and Heshan, ambient formaldehyde could accumulate to over 10 ppbV, which was significantly higher than levels found in other observations (Li et al., 2013; Chen et al., 2014). Another possible explanation is unmeasured species, either primary hydrocarbons or secondary products, which will be discussed in later sessions.

4.2 Contributions to the missing reactivity: primary VOCs

As missing reactivity was observed at Beijing and Heshan site, the species possibly causing these missing were examined. Throughout the whole campaign at the PKU site, missing reactivity was normally found in the morning, as for an example in August 16th and 17th 2013 in (Fig 11). Between 5 a.m. to 10 a.m., local vehicle-related sources were strong, and the chemical reactions were not active yet, and the oxidants levels thus the secondary VOC species remained low. We assumed that the unmeasured primary VOCs species could most likely be the major contributors to missing reactivity. Special attention was paid to the unmeasured branched-alkenes for their high reactivity and was previously observed from vehicle exhaust (Nakashima et al., 2010) and gasoline evaporation emissions (Wu et al., 2015). We found only one dataset of branched alkenes measurements in 2005 measured by NOAA (Liu et al., 2009). We chose the diurnal patterns of missing reactivity in Beijing in 2013 and compared to the diel cycles of four measured branched-alkenes in 2005. The correlations were found as presented in Fig 11. Considering the contribution of the 4 branched alkenes, the VOCs reactivity could be enhanced by 2.3 s^{-1}. This could only partially explain the missing VOCs reactivity which was around 10 s^{-1}. With observed decreasing trends in mixing ratios of most NMHCs species in Beijing (Zhang et al., 2014; Wang et al., 2015), the branched-alkenes were insufficient to tell the full story of the missing reactivity. Unmeasured semi-volatile organic compounds (SVOCs) and intermediate volatile organic compounds (IVOCs), such as alkanes between C12 to C30, and polycyclic aromatic hydrocarbons (PAHs) could be also important. Sheehy (2010) found SVOCs and IVOCs contributed to about 10% in morning time in Mexico City. Future studies with a wider range of reactive VOCs measurement for total OH reactivity closure is needed.

4.3 Contributions to the missing reactivity: secondary VOCs

Due to limitations in chemistry mechanisms as well as measuring techniques, secondary products are not fully quantified in ambient air and could probably contribute significantly to the observed missing reactivity, especially in the urban or suburban sites receiving chemically complex aged air masses.

Besides the large missing reactivity during the morning rush hour, there was about 25% difference between measured and calculated reactivity from August 16th to 18th, 2013 at PKU site. Considering high levels of oxidants in daytime, the mixing ratios of branched-alkenes could be lower than 0.1 ppbV, which could not explain the observed missing reactivity. A box model was deployed to investigate the role of secondary species in variation of VOCs reactivity. The model, constrained by measured parameters (meteorology, inorganic gases, VOCs including measured carbonyls), gave the results of VOCs reactivity which agreed well with the measured reactivity in most of the daytime (Fig 11). Major contributors from modeled species were unmeasured aldehydes, glyoxal and methyl glyoxal. Average values of major secondary contributors to modelled reactivity were provided in Table S5. However, the missing in morning hours remain unsolved: In the model run, the higher secondary contribution on August 17th 2013 morning was owing to isoprene oxidation products, by using 1.5 ppbv of isoprene levels as model input, the missing reactivity kept over 40% around 7:00 and 8:00 a. m.

The similar model was applied for the Heshan observation (Fig 12). During the polluted episode between October 24th and 27th 2014, a 30% missing reactivity existed for most time. Unfortunately, the modeled reactivity was only 10-20% higher than calculated reactivity, and not enough to explain the measured reactivity. The major contributors among modeled species were also unmeasured aldehydes, glyoxal, methyl glyoxal and other secondary products, as shown in Table S6. Due to strong emissions of aromatics from solvent use and petroleum industry in PRD region (Zheng et al., 2009), high levels of glyoxal and methyl glyoxal in this region were observed from satellite measurement (Liu et al., 2012) and ground measurements (Li et al., 2013). Compared to the 2006 measurements in Back garden, a semi-rural site in PRD region, the modeled glyoxal was twice as high as around 0.8 ppbV (Li et al., 2013). This difference possibly resulted from higher levels of precursors in 2014 measurements, where the measured reactivity was about 50% higher than the results in Backgarden 2006 (Lou et al., 2010).

4.4 Implications for ozone production efficiency

The investigating of missing in VOCs reactivity is expected to better understand the ozone formation processes. To evaluate this contribution, we employed the box model to calculate the influence of VOCs reactivity on OPE. We set two scenarios for the model run: 1) The base run was constrained with measured species, including all inorganic compounds, PAMS 56 hydrocarbons, TO-15 OVOCs and formaldehyde. This is how we obtained the modelled reactivity as presented above, and the intermediates and oxidation products were reproduced as well. 2) The other scenario used measured reactivity as a constraint. Due to the difference between measured and modeled reactivity, we allocated the missing reactivity into several groups. For the primary species, we assumed the ratio between total chain-alkenes and branched-alkenes were the same in Beijing 2013 and in Heshan 2014 as the ratio in Beijing 2005, so we got the assumed mixing ratios of branched-alkenes at both sites. For secondary species, we allocated the remaining missing reactivity into different intermediates or products based on weights obtained in the model base run. Under both assumptions, we ran the OBM and calculated the OPE, as presented in Fig 13.

For both sites, the OPE constrained by measured reactivity were significantly higher than the OPE we calculated from modeled reactivity. In Beijing, the OPE from measured reactivity was about 21% higher on average. The value was 30% higher at Heshan site under similar assumptions. This percentage was close to the percentage of missing reactivity, indicating the ignorance of unmeasured or unknown organic species can cause significant underestimation in ozone production calculation.

Compared to other similar calculations worldwide, the OPE results for Beijing and Heshan were significantly higher (Fig 14). The comparison was made for NO_x = 20 ppbV which was in the range of most observation results. For urban measurements, only the results from Mexico City in MCMA-03 were close to the Beijing results in basic model run (Lei et al., 2008). For suburban measurements, the OPE in Heshan 2014 was higher than all other three campaigns, even including the results from Shangdianzi station in CAREBEIJING-2008 campaigns (Ge et al., 2012). While taking missing reactivity into consideration, the OPE results were even higher, indicating more ozone was produced by the reactions of the same quantity of NO_x

molecules.

5. Conclusions

In this study, total OH reactivity measurements employing CRM system were conducted at PKU site in Beijing 2013, and Heshan site 2014 in PRD region. Comparisons between measured and calculated, as well as modelled reactivity were made and possible reasons for the missing reactivity have been investigated. The contribution of missing reactivity to ozone production efficiency was evaluated.

In Beijing 2013, daily median result for measured total OH reactivity was 20 ± 11 s^{-1}. Similar diurnal variation with other urban measurements was found with peaks over 25 s^{-1} during the morning rush hour and lower reactivity than 16 s^{-1} in the afternoon. In Heshan 2014, total OH reactivity was 31 ± 20 s^{-1} on daily median result. The diurnal variation was not significant. Both sites have experienced OH reactivity over 80 s^{-1} during polluted episodes.

Missing reactivity was found at both sites. While in Beijing the missing reactivity made up 21% of measured reactivity, some periods even reached a higher missing percentage as 40%-50%. In Heshan, missing reactivity's contribution to total OH reactivity was 32% on average and quite stable for the whole day. Unmeasured primary species, such as branched-alkenes could be important contributor to the missing reactivity in Beijing, especially in morning rush hour, but they were not enough to explain Aug 17th morning's event. With the help of RACM2, unmeasured secondary products were calculated and thus the modelled reactivity could agree with measured reactivity in Beijing in the noontime. However, they were still not enough to explain the missing reactivity in Heshan, even in daytime. This was probably because of the relatively higher oxidation stage in Heshan than in Beijing.

Missing reactivity could impact the estimation of atmospheric ozone production efficiency. Compared to modeled reactivity from base run, ozone production efficiency would rise 21% and 30% in Beijing and Heshan with measured reactivity applied. Both results were significantly higher than similar observations worldwide, indicating the relatively faster ozone production at both sites.

However, in order to further explore the OH reactivity in both regions, more efforts should be paid in both OH reactivity measurements and speciated measurements, as well as modeling to close the total OH reactivity budget. Moreover, a thorough way with more detailed mechanisms should be established to connect the missing reactivity to the evaluation of ozone production.

Acknowledgement

This study was funded by the National Key Research and Development Plan (grant no. 2016YFC020200), Natural Science Foundation for Outstanding Young Scholars (grant no. 41125018) and a Natural Science Foundation key project (grant no.411330635). The research was also supported by the European Commission Partnership with China on Space Data (PANDA project). Special thanks to Jing Zheng, Mei Li, Yuhan Liu from Peking University and Tao Zhang from Guangdong Environmental Monitoring Center for the help, thanks for William. C. Kuster from NOAA . Earth System Research Laboratory for the branched-alkenes data in 2005.

Reference

Barletta, B., Meinardi, S., Sherwood Rowland, F., Chan, C.-Y., Wang, X., Zou, S., Yin Chan, L., and Blake, D. R.: Volatile organic compounds in 43 Chinese cities, Atmos. Environ., 39, 5979-5990, doi: 10.1016/j.atmosenv.2005.06.029, 2005.

Calpini, B., Jeanneret, F., Bourqui, M., Clappier, A., Vajtai, R., and van den Bergh, H.: Direct measurement of the total reaction rate of OH in the atmosphere, Analusis, 27, 328-336, doi: 10.1051/analusis:1999270328, 1999.

Chatani, S., Shimo, N., Matsunaga, S., Kajii, Y., Kato, S., Nakashima, Y., Miyazaki, K., Ishii, K., and H., U.: Sensitivity analyses of OH missing sinks over Tokyo metropolitan area in the summer of 2007, Atmos. Chem. Phys., 9, 8975-8986, doi:

10.5194/acp-9-8975-2009, 2009.

Chen, W. T., Shao, M., Lu, S. H., Wang, M., Zeng, L. M., Yuan, B., Liu, Y.: Understanding primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF model. Atmos. Chem. Phys., 14, 3047-3062, doi: 10.5194/acp-14-3047-2014, 2014.

Chou, C. C. K., Tsai, C. Y., Chang, C. C., Lin, P. H., Liu, S. C., and Zhu, T.: Photochemical production of ozone in Beijing during the 2008 Olympic Games, Atmos. Chem. Phys., 11, 9825-9837, doi: 10.5194/acp-11-9825-2011, 2011.

Dodge, M. C.: Proceedings of the international conference on photochemical oxidant pollution and its control. Combined use of modeling techniques and smog chamber data to derive ozone-precursor relationships, U.S. Environmental Protection Agency, Research Triangle Park, NC, 881-889 pp., 1977.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophy. Res.-Atmos., 110, D16305, doi: 10.1029/2004jd005623, 2005.

Dolgorouky, C., Gros, V., Sarda-Esteve, R., Sinha, V., Williams, J., Marchand, N., Sauvage, S., Poulain, L., Sciare, J., and Bonsang, B.: Total OH reactivity measurements in Paris during the 2010 MEGAPOLI winter campaign, Atmos. Chem. Phys., 12, 9593-9612, doi: 10.5194/acp-12-9593-2012, 2012.

Edwards, P. M., Evans, M. J., Furneaux, K. L., Hopkins, J., Ingham, T., Jones, C., Lee, J. D., Lewis, A. C., Moller, S. J., Stone, D., Whalley, L. K., and Heard, D. E.: OH reactivity in a South East Asian tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project, Atmos. Chem. Phys., 13, 9497-9514, doi: 10.5194/acp-13-9497-2013, 2013.

Fang, X., Shao, M., Stohl, A., Zhang, Q., Zheng, J., Guo, H., Wang, C., Wang, M., Ou, J., Thompson, R. L., and Prinn, R. G.: Top-down estimates of benzene and toluene emissions in the Pearl River Delta and Hong Kong, China, Atmos. Chem. Phys., 16, 3369-3382, doi: 10.5194/acp-16-3369-2016, 2016.

Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H. P., Häseler, R., Holland, F., Kaminski, M., Li, X., Lu, K., Nehr, S., Tillmann, R., Wegener, R., and Wahner, A.: Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, Nature Geoscience, 6, 1023-1026, doi: 10.1038/ngeo1964, 2013.

Fuchs, H., Tan, Z. F., Lu, K. D., Bohn, B., Broch, B., Brown, S. S., Dong, H. B., Gomm. S., Haseler, H. L. Y., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Lu, S. H., Min, K.-E., Rohrer, F., Shao, M., Wang, B. L., Wang, M., Wu, Y. S., Zeng, L. M., Zhang, Y. S., Wahner, A., Zhang, Y. H.: OH reactivity at a rural site (Wangdu) in the North China Plain: Contributions from OH reactants and experimental OH budget, Atmos. Chem. Phys., Dis., 716-745, doi: 10.5194/acp-2016-716, 2016.

Ge. B. Z., Sun. Y. L., Liu. Y., Dong. H. B., Ji. D. S., Jiang. Q., Li. J., Wang. Z. F.: Nitrogen dioxide measurement by cavity attenuated phase shift spectroscopy (CAPS) and implications in ozone production efficiency and nitrate formation in Beijing, China. J. Geophy. Res.-Atmos., 118, 9499-9509, doi: 10.1002/jgrd.50757, 2013.

Geddes, J. A., Murphy, J. G., and K., W. D.: Long term changes in nitrogen oxides and volatile organic compounds in Toronto and the challenges facing local ozone control, Atmos. Environ., 43, 3407-3415, doi: 10.1016/j.atmosenv.2009.03.053, 2009.

Geiger, H., Barnes, I., Bejan, I., Benter, T., and Spittler, M.: The tropospheric degradation of isoprene: an updated module for the regional atmospheric chemistry mechanism, Atmos. Environ., 37, 1503–1519, doi: 10.1016/S1352-2310(02)01047-6, 2003.

Goliff, W. S., Stockwell, W. R., Lawson, C. V.: The regional atmospheric chemistry mechanism, version 2. Atmos. Environ., 68, 174-185, doi: 10.1016/j.atmosenv.2012.11. 038, 2013

Hansen, R. F., Blocquet, M., Schoemaecker, 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., 8, 4243-4264, doi: 10.5194/amt-8-4243-2015, 2015.

Ingham, T., Goddard, A., Whalley, L. K., Furneaux, K. L., Edwards, P. M., Seals, C. P., Self, D. E., Johnson, G. P., Read, K. A., Lee, J. D., and E., H. D.: a flow tube based LIF instrument to measure OH reactivity in the troposphere, Atmos. Meas. Tech., 2, 465-477, doi: 10.5194/amt-2-465-2009, 2009.

Karl, M., Dorn, H.-P., Holland, F., Koppmann, R., Poppe, D., Rupp, L., Schaub, A., and Wahner, A.: Product study of the reaction of OH radicals with isoprene in the atmosphere simulation chamber SAPHIR, J. Atmos. Chem., 55, 167–187, doi: 10.1007/s10874-006-9034-x, 2006.

Kato, S, Sato, T., Kaji, Y.: A method to estimate the contribution of unidentified VOCs to OH reactivity. Atmos. Environ., 45, 5531-5539, doi: 10.1016/j.atmosenv.2011.05. 074. 2011.

Kleinman, L. I., Daum, P. H., Imre, D. G., Lee. J. H., Lee. Y. N., Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., Newman, L.: Ozone production in the New York City urban plume. J. Geophy. Res.-Atmos., 105, D11, 14495-14511, doi: 10.1029/2000 jd900011, 2000.

Kleinman, L. I.: Ozone production efficiency in an urban area, J. Geophy. Res. – atmos., 107, D23, 4733, doi: 10.1029/2002jd002529, 2002.

Kovacs, T. A., and Brune, W. H.: Total OH loss rate measurement, J. Atmos. Chem., 39, 105-122, doi: 10.1023/a:1010614113786, 2001.

Kovacs, T. A., Brune, W. H., Harder, H., Martinez, M., Simpas, J. B., Frost, G. J., Williams, A. G., Jobson, B. T., Stroud, C., Young, V., Fried, A., and B., W.: Direct measurements of urban OH reactivity during Nashville SOS in summer 1999, J. Environ. Monit., 5, 68-74, doi: 10.1039/b204339d, 2003.

Kumar V., Sinha, V.: VOC-OHM: a new technique for rapid measurements of ambient total OH reactivity and volatile organic compounds using a single proton transfer reaction mass spectrometer. Int. J. of Mass Spectrom., 374, 55-63. 2014.

LaFranchi, B. W., Goldstein, A. H., and Cohen, R. C.: Observations of the temperature dependent response of ozone to NO_x reductions in the Sacramento, CA urban plume, Atmos. Chem. Phys., 11, 6945-6960, doi: 10.5194/acp-11-6945-2011, 2011.

Lee, J. D., Young, J. C., Read, K. A., Hamilton, J. F., Hopkins, J. R., Lewis, A. C., Bandy, B. J., Davey, J., Edwards, P. M., Ingham, T., Self, D. E., Smith, S. C., Pilling, M. J., and Heard, D. E.: Measurement and calculation of OH reactivity at a United Kingdom coastal site, J. Atmos. Chem., 64, 53-76, doi: 10.1007/s10874-010-9171-0, 2010.

Lei, W., Zavala, M., Foy, B. de., Volkamer, R., Molina, L. T.: Characterizing ozone production and response under different meteorological conditions in Mexico City. Atmos. Chem. Phys., 8, 7571-7581, doi: 10.5194/acp-8-7571-2008, 2008.

Li, M., Shao, M., Li, L.-Y., Lu, S.-H., Chen, W.-T., and Wang, C.: Quantifying the ambient formaldehyde sources utilizing tracers, Chinese. Chem. Lett., 25, 1489-1491, doi: 10.1016/j.cclet.2014.07.001, 2014.

Li, X., Brauers, T., Hofzumahaus, A., Lu, K., Li, Y. P., Shao, M., Wagner, T., and Wahner, A.: MAX-DOAS measurements of NO_2, HCHO and CHOCHO at a rural site in Southern China, Atmos. Chem. Phys., 13, 2133-2151, doi: 10.5194/acp-13-2133-2013, 2013.

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., and Tang, D.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42, 6247-6260, doi: 10.1016/j.atmosenv.2008.01.070, 2008.

Liu, Y., Shao, M., Kuster, W. C., Goldan, P. D., Li, X. H., Lu, S. H., de Gouw, J. A.: Source identification of reactive hydrocarbons and oxygenated VOCs in the summertime in Beijing. Environ. Sci. Technol., 43, 75-81, doi: 10.1021/es801716n, 2009.

Liu, Y. H., Lu, K. D., Dong, H. B., Li, X., Cheng, P., Zou, Q., Wu, Y. S., Liu, X. G., Zhang, Y. H. In situ monitoring of atmospheric nitrous acid based on multi-pumping flow system and liquid waveguide capillary cell. J. Envion. Sci. Accepted. 2016.

Liu, Z., Wang, Y., Vrekoussis, M., Richter, A., Wittrock, F., Burrows, J. P., Shao, M., Chang, C.-C., Liu, S.-C., Wang, H., and Chen, C.: Exploring the missing source of glyoxal (CHOCHO) over China, Geophy. Res. Lett., 39, L10812, doi: 10.1029/2012gl051645, 2012.

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Häseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results, Atmos. Chem. Phys., 10, 11243-11260, doi: 10.5194/acp-10-11243-2010, 2010.

Lu, K. D., Zhang, Y. H., Su, H., Brauers, T., Chou, C. C., Hofzumahaus, A., Liu, S. C., Kita, K., Kondo, Y., Shao, M., Wahner, A., Wang, J. L., Wang, X., and T., Z.: Oxidant (O_3+ NO_2) production processes and formation regimes in Beijing, J. Geophys. Res.-Atmos., 115, D07303, doi: 10.1029/2009jd012714, 2010.

Lu, K. D., Hofzumahaus, A., Holland, F., Bohn, B., Brauers, T., Fuchs, H., Hu, M., Häseler, R., Kita, K., Kondo, Y., Li, X., Lou, S. R., Oebel, A., Shao, M., Zeng, L. M., Wahner, A., Zhu, T., Zhang, Y. H., and Rohrer, F.: Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO_2 concentrations in summer 2006, Atmos. Chem. Phys., 13, 1057-1080, doi: 10.5194/acp-13-1057-2013, 2013.

Mao, J. Q., Ren, X. R., Chen, S., Brune, W. H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappengluck, B., Flynn, J., and M., L.: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, Atmos. Environ., 44, 4107-4115, doi: 10.1016/j.atmosenv.2009.01.013, 2010.

Michoud, V., Hansen, R. F., Locoge, N., Stevens, P. S., and Dusanter, S.: Detailed characterizations of the new Mines Douai comparative reactivity method instrument via laboratory experiments and modeling, Atmos. Meas. Tech., 8, 3537-3553, doi: 10.5194/amt-8-3537-2015, 2015.

Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H. G., Vilà-Guerau de Arellano, J., and Lelieveld, J.: Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010, Atmos. Chem. Phys., 12, 8257-8270, doi: 10.5194/acp-12-8257-2012, 2012.

Nölscher, A. C., Yanez-Serrano, A. M., Wolff, S., de Araujo, A. C., Lavric, J. V., Kesselmeier, J., and Williams, J.: Unexpected seasonality in quantity and composition of Amazon rainforest air reactivity, Nature communications, 7, 10383-10394, doi: 10.1038/ncomms10383, 2016.

Nakashima, Y., Kamei, N., Kobayashi, S., and Y., K.: Total OH reactivity and VOC analyses for gasoline vehicular exhaust with a chassis dynamometer, Atmos. Environ., 44, 468-475, doi: 10.1016/j.atmosenv.2009.11.006, 2010.

Pöschl, U., von Kuhlmann, R., Poisson, N., and Crutzen, P. J.: Development and intercomparison of condensed isoprene oxidation mechanisms for global atmospheric modeling, J. Atmos. Chem., 37, 29–52, doi: 10.1023/A:1006391009798, 2000.

Ren, X. R., Harder, H., Martinez, M., Lesher, R. L., Oliger, A., Shirley, T., Adams, J., Simpas, J. B., and H., B. W.: HO_x concentrations and OH reactivity observations in New York City during PMTACS-NY2001, Atmos. Environ., 37, 3627-3637, doi: 10.1016/s1352-2310(03)00460-6, 2003.

Ren, X. R., Brune, W. H., Cantrell, C., Edwards, G. D., Shirley, T., Metcalf, A. R., and L., L. R.: Hydroxyl and Peroxy Radical Chemistry in a Rural Area of Central Pennsylvania: Observations and Model Comparisons, J. Atmos. Chem., 52, 231-257, doi: 10.1007/s10874-005-3651-7, 2005.

Ren, X. R., Brune, W. H., Mao, J. Q., Mitchell, M. J., Lesher, R. L., Simpas, J. B., Metcalf, A. R., Schwab, J. J., Cai, C., and Y., L.: Behavior of OH and HO_2 in the winter atmosphere in New York City, Atmos. Environ. 40, 252-263, doi: 10.1016/j.atmosenv. 2005.11.073, 2006a.

Ren, X. R., Brune, W. H., Oliger, A., Metcalf, A. R., Simpas, J. B., Shirley, T., Schwab, J. J., Bai, C., Roychowdhury, U., Li, Y., Cai, C., Demerjian, K. L., He, Y., Zhou, X. H., Gao, H., and J., H.: OH, HO_2, and OH reactivity during the PMTACS–NY Whiteface Mountain 2002 campaign: Observations and model comparison, J. Geophys. Res.-Atmos., 111, doi: 10.1029/2005jd006126, 2006b.

Sadanaga, Y., Yoshino, A., Kato, S., Yoshioka, A., Watanabe, K., Miyakawa, T., Hayashi, I., Ichikawa, M., Matsumoto, J., Nishiyama, A., Akiyama, N., Kanaya, Y., and Y., K.: The importance of NO_2 and volatile organic compounds in the urban air from the viewpoint of the OH reactivity, Geophy. Res. Lett., 31, L08102, doi: 10.1029/2004gl019661, 2004.

Sadanaga, Y., Yoshino, A., Kato, S., and Y., K.: measurements of OH reactivity and photochemical ozone production in the urban atmosphre, Environ. Sci. Technol., 39, 8847-8852, doi: 10.1021/es049457p, 2005.

Sheehy, P. M., Volkamer, R., Molina, L. T., and Molina, M. J.: Oxidative capacity of the Mexico City atmosphere – Part 2: A RO_x radical cycling perspective, Atmos. Chem. Phys., 10, 6993-7008, doi: 10.5194/acp-10-6993-2010, 2010.

Shirley, T. R., Brune, W. H., Ren, X. R., Mao, J. Q., Lesher, R., Cardenas, B., Volkamer, R., Molina, L. T., Molina, M. J., Lamb, B., Velasco, E., Jobson, T., and M., A.: Atmospheric oxidation in the MCMA during April 2003, Atmos. Chem. Phys., 6, 2753-2765, doi: 10.5194/acp-6-2753-2006, 2006.

Sinha, V., Williams, J., Crowley, J. N., and J., L.: The Comparative Reactivity Method - a new tool to measure total OH reactivity in ambient air, Atmos. Chem. Phys., 8, 2213-2227, doi: 10.5194/acp-8-2213-2008, 2008.

Sinha, V., Custer, T. G., Kluepfel, T., and Williams, J.: The effect of relative humidity on the detection of pyrrole by PTR-MS for OH reactivity measurements, Int. J. Mass Spectrom., 282, 108-111, doi: 10.1016/j.ijms.2009.02.019, 2009.

Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kalos, M. K., Patokoski, L., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, L., and M., K.: OH reactivity measurements within a boreal forest - evidence for unknown reactive emissions, Environ. Sci. Technol., 44, 6614-6620, doi: 10.1021/es101780b, 2010.

Sinha, V., Williams, J., Diesch, J. M., Drewnick, F., Martinez, M., Harder, H., Regelin, E., Kubistin, D., Bozem, H., Hosaynali-Beygi, Z., Fischer, H., Andrés-Hernández, M. D., Kartal, D., Adame, J. A., and Lelieveld, J.: Constraints on instantaneous ozone production rates and regimes during DOMINO derived using in-situ OH reactivity measurements, Atmos. Chem. Phys., 12, 7269-7283, doi: 10.5194/acp-12-7269-2012, 2012.

Stockwell, W. R., Kirchner, F., Kuhn, M., and Seefeld, S.: A new mechanism for regional atmospheric chemistry modeling, J. Geophys. Res.-Atmos., 102, D22, 25847-25879, doi: 10.1029/97jd00849, 1997.

Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO_2 radicals: field measurements and model comparisons, Chem. Soc. Rev., 41, 6348-6404, doi: 10.1039/c2cs35140d, 2012.

Tan, Z. F., Fuchs, H., Zhang, Y. H., et al., Atmos. Chem. Phys., in preparation.

Wang, M., Zeng, L., Lu, S., Shao, M., Liu, X., Yu, X., Chen, W., Yuan, B., Zhang, Q., Hu, M., and Zhang, Z.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, Anal. Methods, 6, 9424-9434, doi: 10.1039/c4ay01855a, 2014a.

Wang, M., Shao, M., Chen, W. T., Yuan, B., Lu, S. H., Zhang, Q., Zeng, L. M., Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China. Atmos. Chem. Phys. 14, 5871-5891, doi: 10.5194/acp-14-5871-2014, 2014b.

Wang, M., Shao, M., Chen, W., Lu, S., Liu, Y., Yuan, B., Zhang, Q., Zhang, Q., Chang, C. C., Wang, B., Zeng, L., Hu, M., Yang, Y., and Li, Y.: Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013, Atmos. Chem. Phys., 15, 1489-1502, doi: 10.5194/acp-15-1489-2015, 2015.

Wang, T., Ding, A., Gao, J., and Wu, W. S.: Strong ozone production in urban plumes from Beijing, China. Geophy. Res. Lett., 33, L21806, doi: 10.1029/2006gl027689, 2006.

Whalley, L. K., Stone, D., Bandy, B., Dunmore, R., Hamilton, J. F., Hopkins, J., Lee, J. D., Lewis, A. C., and Heard, D. E.: Atmospheric OH reactivity in central London: observations, model predictions and estimates of in situ ozone production, Atmos. Chem. Phys., 16, 2109-2122, doi: 10.5194/acp-16-2109-2016, 2016.

Williams, J.: Provoking the air, Environ. Chem., 5, 317-319, doi:10.1071/en08048, 2008.

Williams, J., and Brune, W. H.: A roadmap for OH reactivity research, Atmos. Environ., 106, 371-372, doi: 10.1016/j.atmosenv.2015.02.017, 2015.

Williams, J., Keßel, S. U., Nölscher, A. C., Yang, Y. D., Lee, Y. N., Yáñez-Serrano, A. M., Wolff, S., Kesselmeier, J., Klüpfel, T., Lelieveld, J., and Shao, M.: Opposite OH reactivity and ozone cycles in the Amazon rainforest and megacity Beijing: Subversion of biospheric oxidant control by anthropogenic emissions, Atmos. Environ., 125, 112-118, doi: 10.1016/j.atmosenv.2015.11.007, 2016.

Wu, Y., Yang, Y. D., Shao, M., and Lu, S. H.: Missing in total OH reactivity of VOCs from gasoline evaporation, Chinese. Chem. Lett., 26, 1246-1248, doi: 10.1016/j.cclet.2015.05.047, 2015.

Yang, Y., Shao, M., Wang, X., Nölscher, A. C., Kessel, S., Guenther, A., and Williams, J.: Towards a quantitative understanding of total OH reactivity: A review, Atmos. Environ.,134, 147-161, doi: 10.1016/j.atmosenv.2016.03.010, 2016.

Yoshino, A., Sadanaga, Y., Watanabe, K., Kato, S., Miyakawa, Y., Matsumoto, J., and Y., K.: Measurement of total OH reactivity by laser-induced pump and probe technique—comprehensive observations in the urban atmosphere of Tokyo, Atmos. Environ., 40, 7869-7881, doi: 10.1016/j.atmosenv.2006.07.023, 2006.

Yoshino, A., Nakashima, Y., Miyazaki, K., Kato, S., Suthawaree, J., Shimo, N., Matsunaga, S., Chatani, S., Apel, E., Greenberg, J., Guenther, A., Ueno, H., Sasaki, H., Hoshi, J., Yokota, H., Ishii, K., and Kajii, Y.: Air quality diagnosis from comprehensive observations of total OH reactivity and reactive trace species in urban central Tokyo, Atmos. Environ., 49, 51-59, doi: 10.1016/j.atmosenv.2011.12.029, 2012.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, D24302, doi: 10.1029/2012jd018236, 2012.

Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C. C., and Liu, S. C.: Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011, Atmos. Chem. Phys., 14, 6089-6101, doi: 10.5194/acp-14-6089-2014, 2014.

Zhang, Y. H., Su, H., Zhong, L. J., Cheng, Y. F., Zeng, L. M., Wang, X. S., Xiang, Y. R., Wang, J. L., Gao, D. F., and Shao, M.: Regional ozone pollution and observation-based approach for analyzing ozone–precursor relationship during the PRIDE-PRD2004 campaign, Atmos. Environ., 42, 6203-6218, doi: 10.1016/j.atmosenv.2008. 05.002, 2008.

Zhao, C., Wang, Y. H., Zeng, T.,: East China Plains: a "Basin" of ozone pollution, Environ. Sci. Technol., 43, 1911-1915, doi: 10.1021/es8027764, 2009.

Zheng, J. Y., Shao, M., Che, W. W., Zhang, L. J., Zhong, L. J., Zhang, Y. H., Streets, D., Speciated VOC emission inventory and spatial patterns of ozone formation potential in the Pearl River Delta, China. Environ. Sci. Technol. 43, 8580–8586, doi: 10.1021/es901688e, 2009.

Zheng, J. Y., Zhong, L. J., Wang, T., Louie, P. K. K., Li, Z. C.: Ground-level ozone in the Pearl River Delta region: analysis of data from a recently established regional air quality monitoring network. Atmos. Environ. 44, 814-823, doi: 10,1016/j/atmosenv. 2009.11.032, 2010.

Zhao. W., Cohan, D. S., Henderson. B. H.: Slower ozone production in Houston, Texas following emission reductions: evidence from Texas Air Quality Studies in 2000 and 2006. Atmos. Chem. Phys. 14, 2777-2788, doi: 10.5194/acp-14-2777-2014, 2014.

Table 1 Total OH reactivity measurements in urban areas

Campaign	Site	Year	method	$k_{OH(measured)}$ (s^{-1}) [a]	$k_{OH(calculated)}$ (s^{-1} if it is a value) [b]	Measured species [c]	Reference
SOS	Nashville, US	summer, 1999	LIF-flow tube	11.3	7.2	SFO	Kovacs et al., 2001; 2003;
PMTACS-NY 2001	NY, US	summer, 2001	LIF-flow tube	15~25	within 10%	SFO	Ren et al., 2003
PMTACS-NY 2004	NY, US	winter, 2004	LIF-flow tube	18-35	statistically lower	SF	Ren et al., 2006a
MCMA-2003	Mexico City, Mexico	spring, 2003	LIF-flow tube	10~120	30% less than	-[d]	Shirley et al., 2006
TexAQS	Houston, US	summer, 2000	LIF-flow tube	7~12	agree well	SFO	Mao et al., 2010
TRAMP2006	Houston, US	summer, 2006	LIF-flow tube	9-22	agree well	SFOB	Mao et al., 2010
	Tokyo, Japan	2003-2004	LP-LIF	10~100	30% less than	SFOB	Sadanaga et al., 2004; Yoshino et al., 2006
	Tokyo, Japan	summer, 2006	LP-LIF	10~55	30% less than	SFOB	Chatani et al., 2009
	Tokyo, Japan	spring, 2009	LP-LIF	10~35	22% less than	SFOB	Kato et al., 2011
	Tokyo, Japan	winter, 2007, autumn, 2009	LP-LIF	10~80	10~15 less than	SFOB	Yoshino et al., 2012

Table 1 Total OH reactivity measurements in urban areas (continued)

	Mainz, German	summer, 2005	CRM	10.4		-	Sinha et al.,2008
MEGAPOLI	Paris, France	winter, 2010	CRM	10~130	10~54% less than	SO	Dolgorouky et al., 2012
ClearfLo	London, England	summer, 2012	LP-LIF	10-116	20~40%	SFOB	Whalley et al., 2016
	Lille, France	autumn , 2012	CRM, LP-LIF	~70	Reasonable agreement	SFO	Hansen et al., 2015
	Dunkirk, France	summer, 2014	CRM	10-130		-	Michoud et al., 2015

a. For sources from different studies, the measured reactivity was presented as the averaged results, or ranges of diurnal variations, or the ranges of the whole campaign.

b. For sources of different studies, the calculated reactivity was presented within an uncertainty range, as a percentage reduction or s^{-1} reduction.

c. Measured species that have been used for the calculated reactivity (following Lou et al., 2010): S = inorganic compounds (CO, NO_x, SO_2 etc) plus hydrocarbons (including isoprene); F = formaldehyde; O = OVOCs other than formaldehyde; B = BVOCs other than isoprene;

d. “-” means a lack of information regarding what has been measured or how long it has been measured.

Table2 Total OH reactivity measurements in suburban and surrounding areas

Campaign	Site	Year	method	$k_{OH(measured)}$ (s^{-1})	k_{OH}（calculated） (s^{-1} if it is a value)	Measured Species	Reference
	Central Pennsylvania, US	spring, 2002	LIF-flow tube	6.1		-	Ren et al., 2005
PMTACS-NY2002	Whiteface Mountain, US	summer, 2002	LIF-flow tube	5.6	within 10%	-	Ren et al., 2006b
TORCH-2	Weybourne, England	spring, 2004	LIF-flow tube	4.85	2.95	SFO	Ingham et al., 2009 Lee et al., 2010
CareBeijing-2006	Yufa, China	summer, 2006	LP-LIF	10-30	agree well	S	Lu et al., 2010; 2013
PRIDE-PRD	Backgarden, China	summer, 2006	LP-LIF	10~120	50% less than	S	Lou et al., 2010
DOMINO	El Arenosillo, Spain	winter, 2008	CRM	6.3~85		SF	Sinha et al., 2012
		spring, 2013	CRM	53	23	SFOB	Kumar & Sinha., 2014

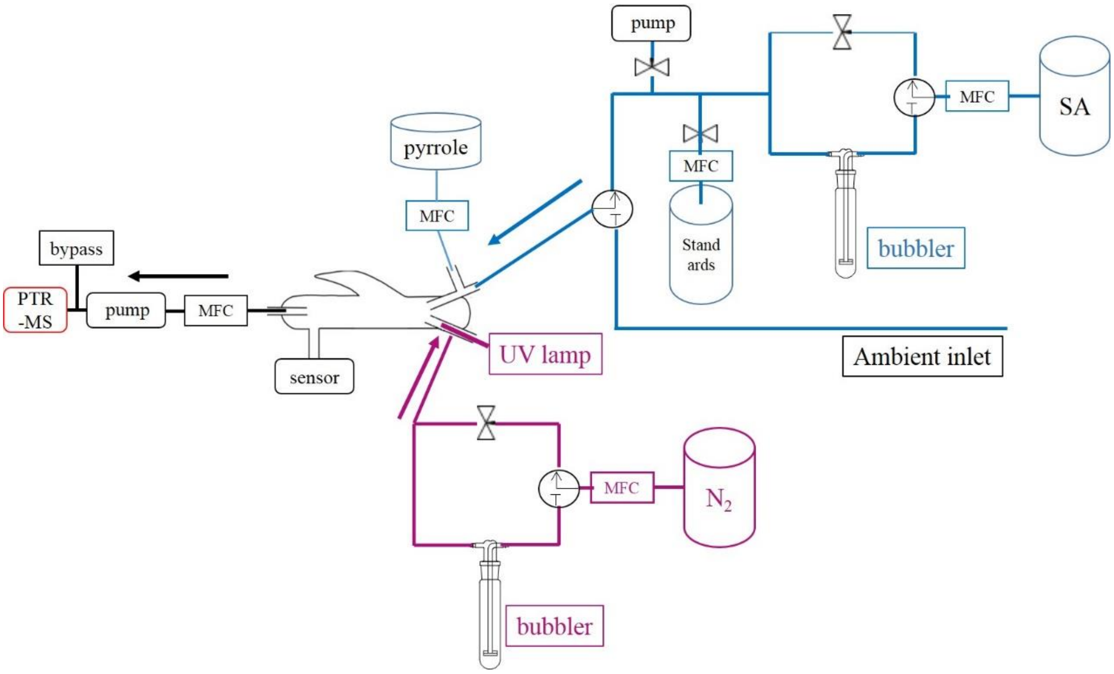


Fig 1 Schematic figures of CRM system in Beijing and Heshan observations. Blue color represents ambient air or synthetic air injection system, purple color represents OH generating system, black color represents the detection system. Pressure is measured by the sensor connected to the glass reaction.

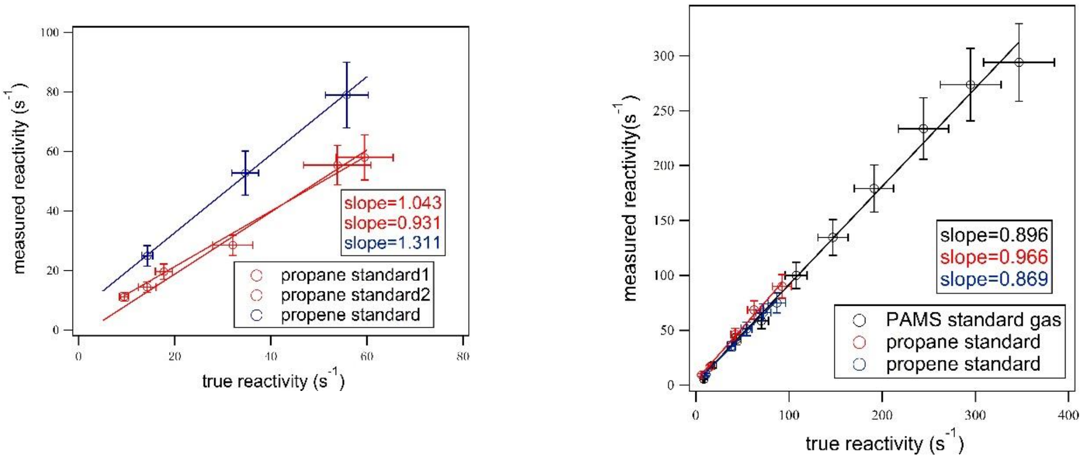


Fig 2 OH reactivity calibration in Beijing (left) and Heshan (right).

Left: Calibration in Beijing used two single standards: propane, propene;

Right: Calibration in Heshan used three standards: propane, propene, mixed PAMS 56 NMHCs.

Error bars stand for estimated uncertainty on the measured and true reactivity.

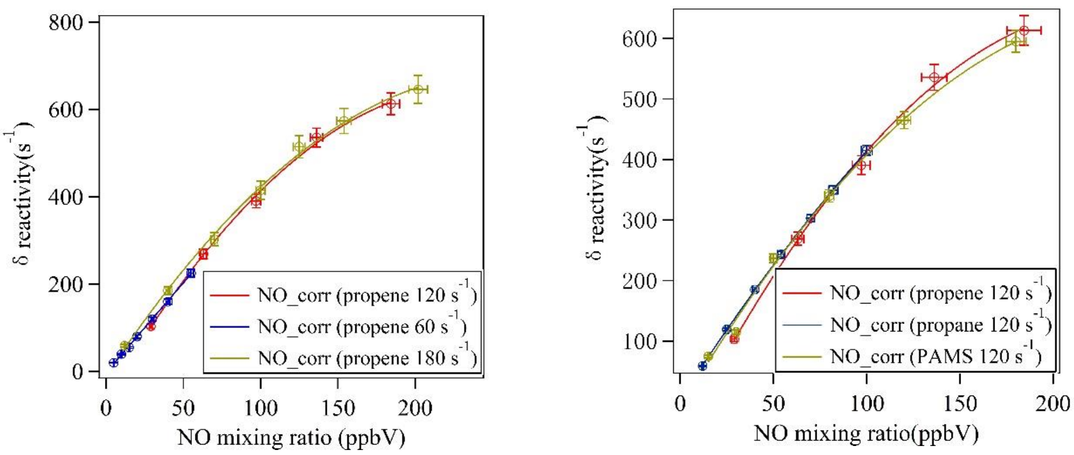


Fig 3 NO-correction experiments and fitting curves in Heshan 2014.

Left: NO-correction experiments with different mixing ratios of propene standard gas;

Right: NO-correction experiments with different standard gases at the same reactivity level: 120 s^{-1}.

Error bars stand for estimated uncertainty on the NO mixing ratios and difference in reactivity.

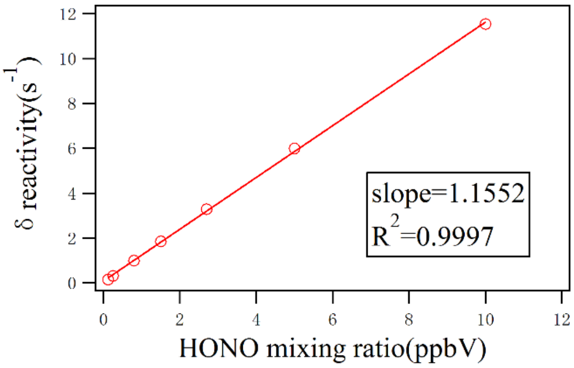


Fig 4 HONO-correction experiments and the fitting curve in Heshan 2014.

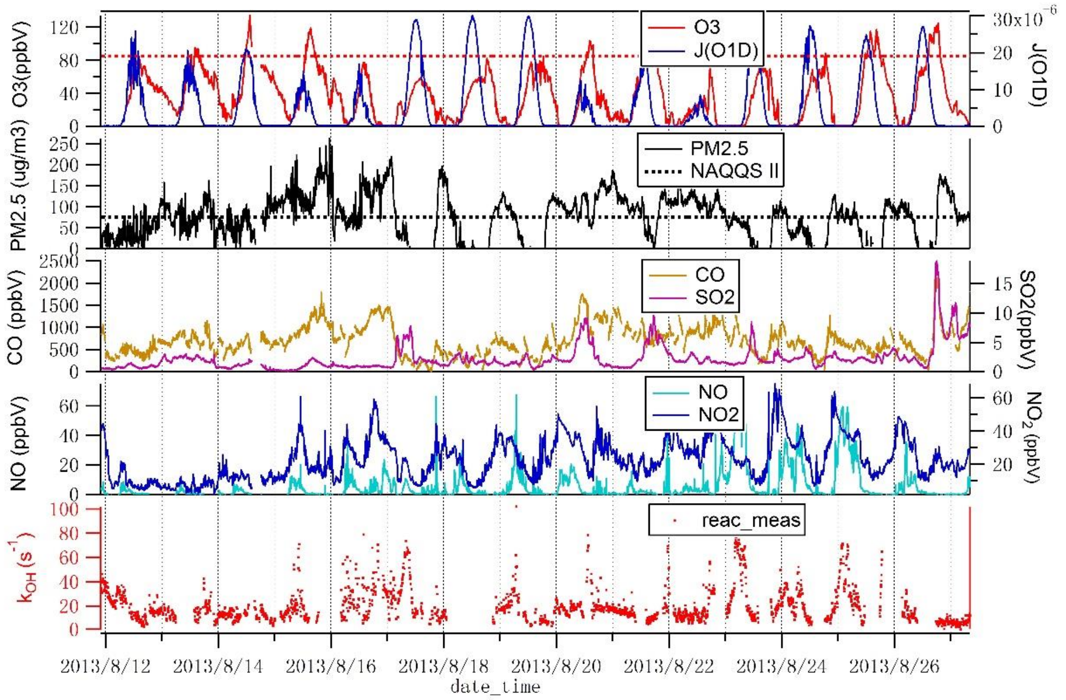


Fig 5-a Time series of meteorological parameters and inorganic trace gases during August 2013 in Beijing.

Red and black dashed lines are Grade II of National Ambient Air Quality Standard.

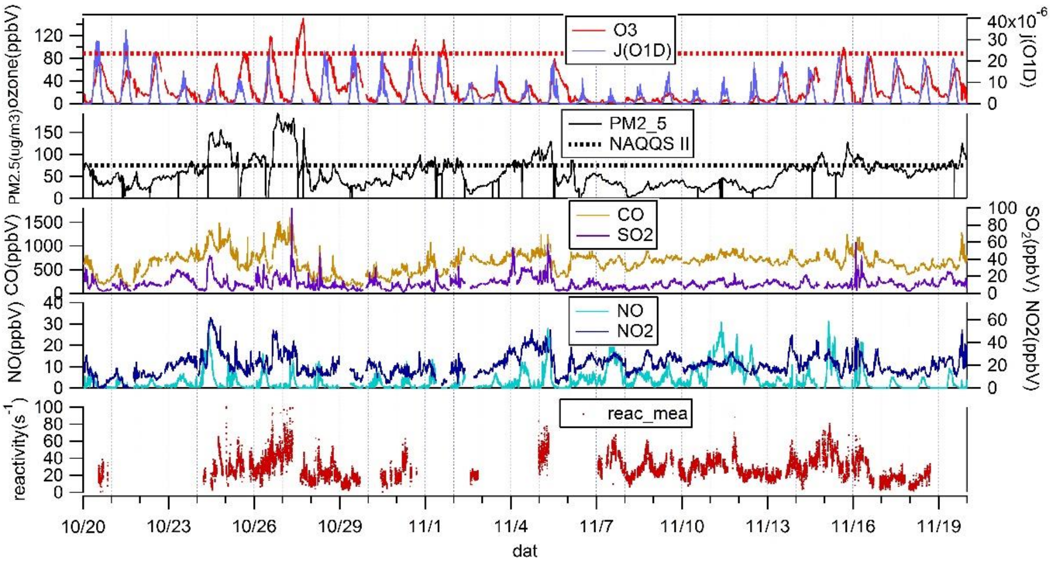


Fig 5-b Time series of meteorological parameters and inorganic trace gases during October-November, 2014 in Heshan.

Red and black dashed lines are Grade II of National Ambient Air Quality Standard.

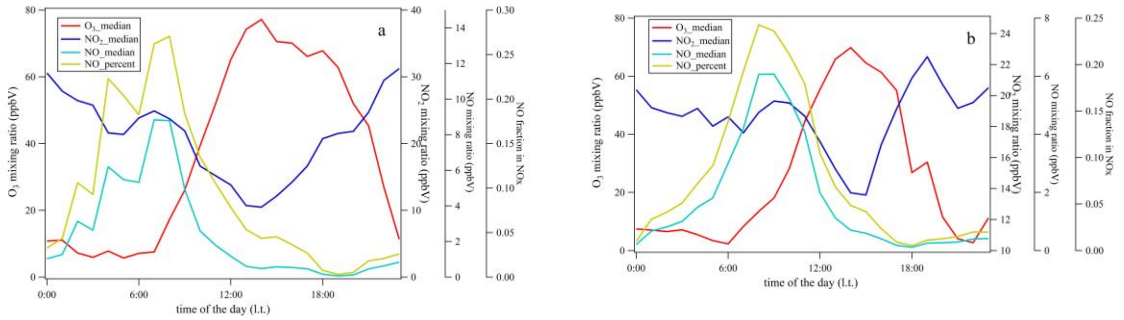


Fig 6 Diurnal variations of O_3, NO, NO_2 and relative contribution of NO to NO_x in Beijing 2013 (a) and Heshan 2014 (b)

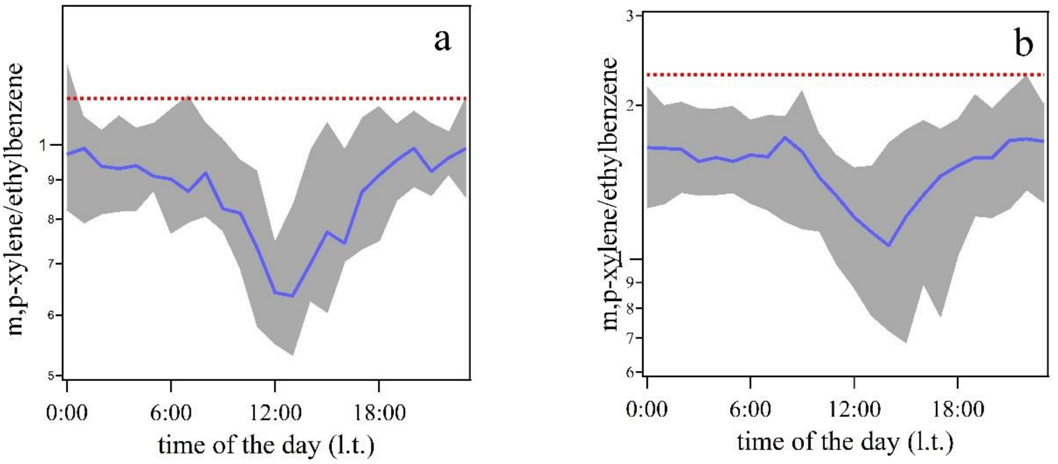


Fig 7 Ratios of m,p-xylene to ethylbenzene in Beijing 2013 (a) and Heshan 2014 (b)

Red dots line: the highest m,p-xylene to ethylbenzene ratio, assumed as emission ratios of m,p-xylene to ethylbenzene, 1.15 ppbV ppbV^{-1} in Beijing 2013 (a) and 2.3 ppbV ppbV^{-1} in Heshan 2014 (b).

Shaded regions: Standard deviation for the ratios during the campaign average.

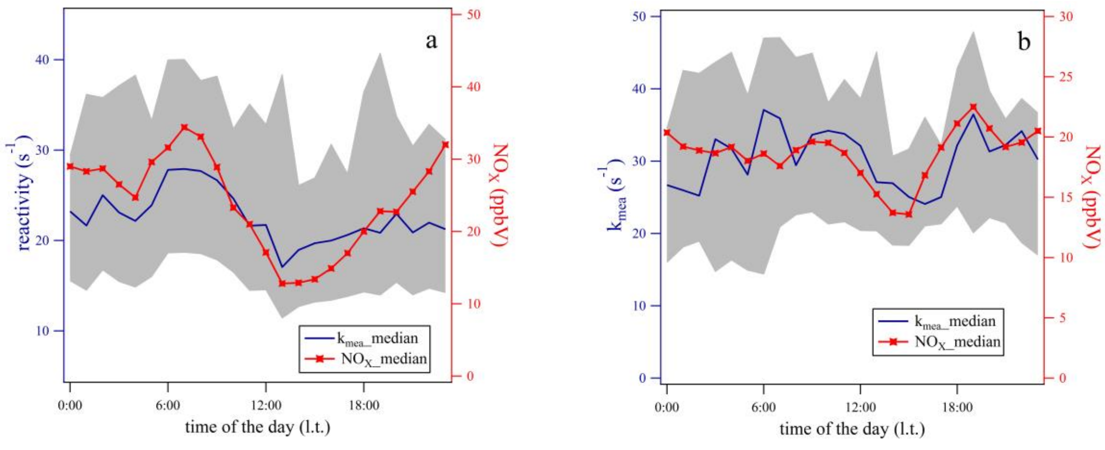


Fig 8 Diurnal variation of hourly median results of measured OH reactivity and NO_x mixing ratios in Beijing (a) and Heshan (b)

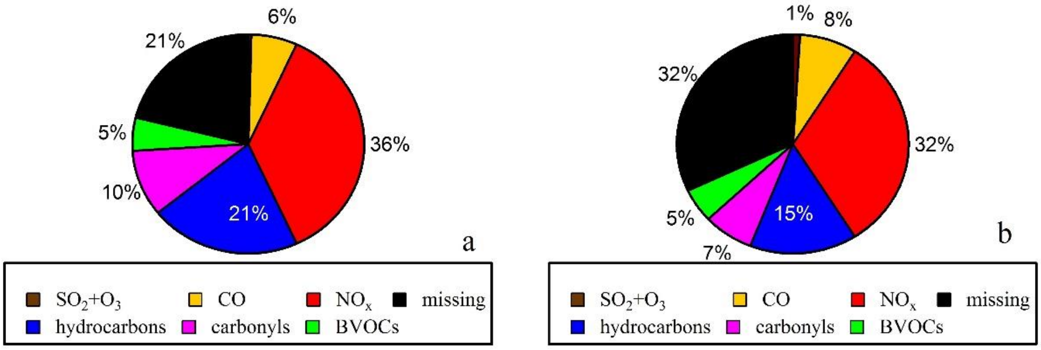


Fig 9 Composition of measured reactivity in Beijing (a) and Heshan (b)

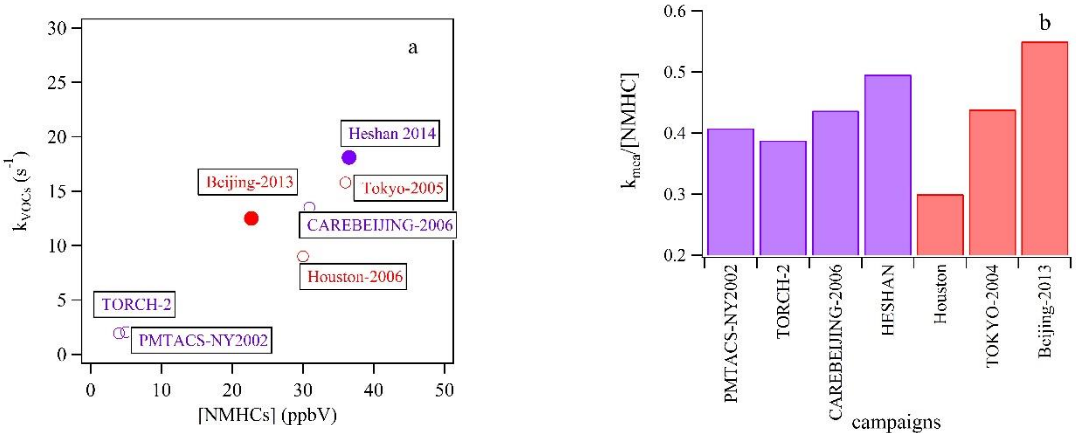


Fig 10 a: Comparison of VOCs reactivity and measured NMHCs in urban and suburban observations.

b: Comparison of the ratio between VOCs reactivity and measured NMHCs in urban and suburban observations

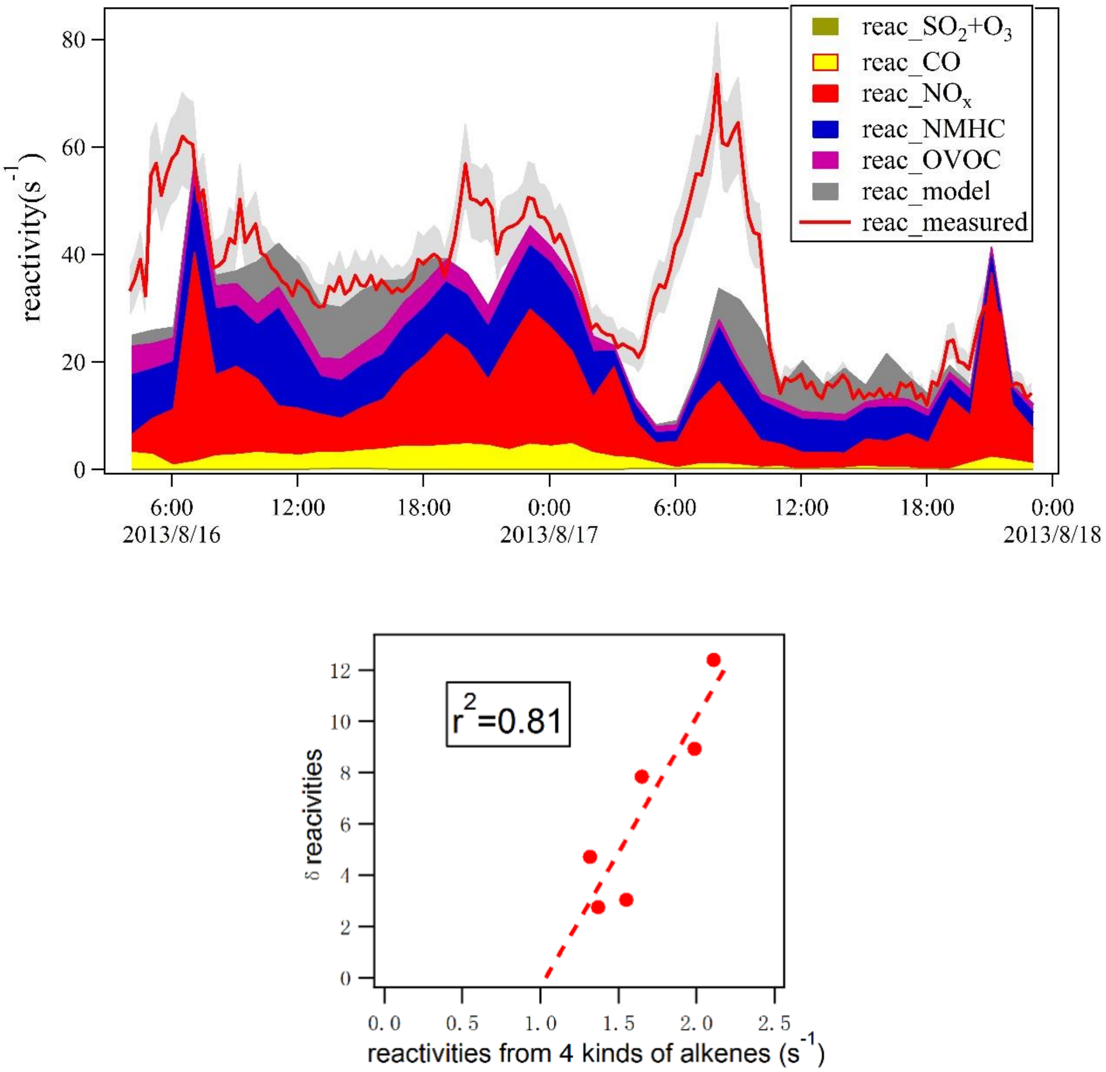


Fig 11 Upper panel: Comparison between measured and calculated reactivity in Beijing August 16th to 18th 2013.

Shallow shaded region: uncertainty of measured reactivity. The same shallow shaded region in Fig 12 represents the same.

Lower panel: Correlation between missing reactivity measured in 2013 and reactivity assumed from branched-chain alkenes from 2005 in diurnal patterns. The 4 branched-alkenes are iso-butene, 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene.

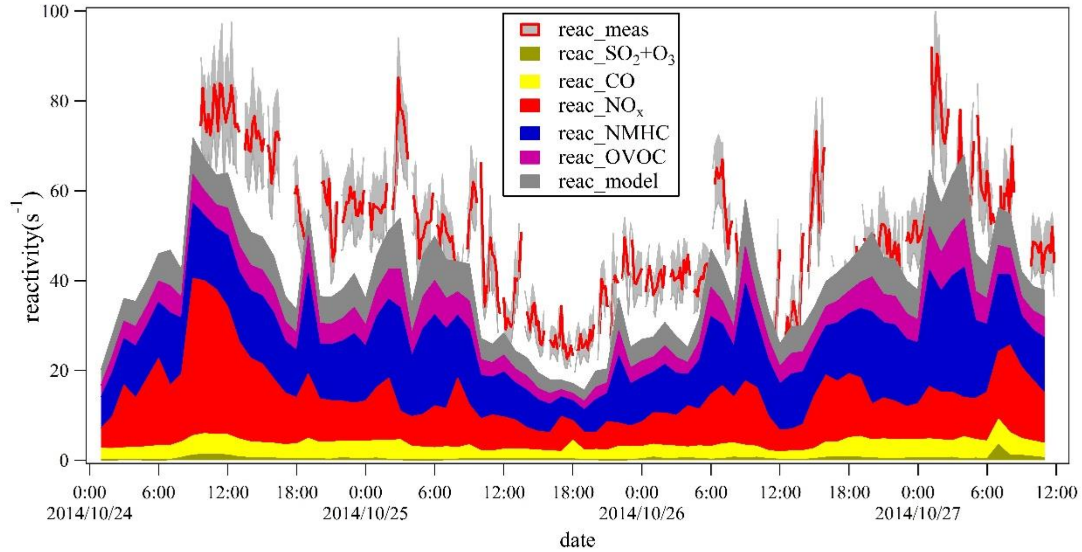
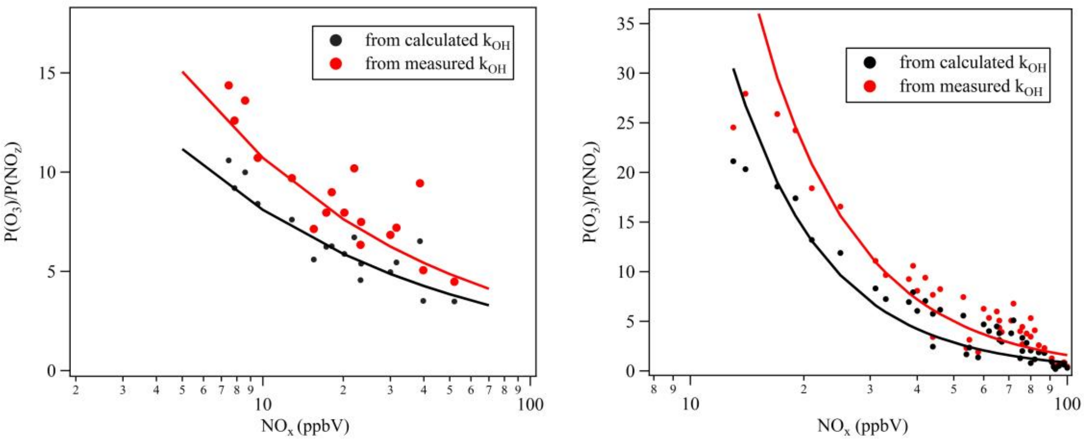


Fig 12 Comparison between measured reactivity and calculated reactivity as well as modelled reactivity in Heshan between October 24th and 27th 2014.



a b

Fig 13 Comparison between OPE calculated from measured reactivity and calculated reactivity in Beijing (a) and Heshan (b).

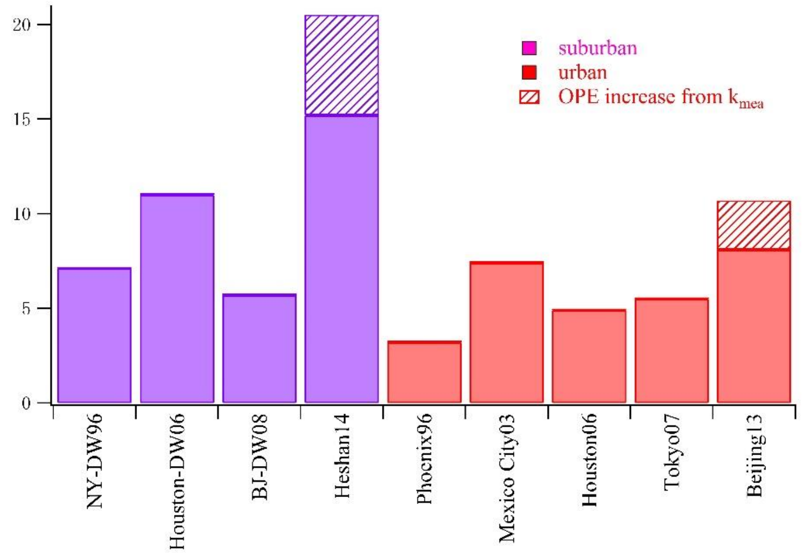


Fig 14 Comparison between the OPE results in this study and other results from literatures. The comparison is made with the NO_x = 20 ppbV. “DW” is in abbreviation of downwind.