Anonymous Referee #1

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The authors present the photochemical oxidation processes simulated by a chemical box model with constraints of field measurement data in four Chinese megacities. The ROx radical budget, OH reactivity, ozone production, and particulate nitrate formation are assessed. The results provide some insights into the formation of secondary pollution such as ozone and nitrate, which are helpful for formulating the air pollution control policy in the polluted regions of China. Hence, this manuscript can be considered for publication after the following comments being properly addressed.

Answer:

We thank the comments and suggestions from the reviewers, which help to improve the manuscript considerably. The response and changes are listed below.

Major Concerns:

A major concern is on the representativeness of measurement results given their relatively short periods, i.e. 1-2 weeks in each city. Are the measured conditions of ozone pollution and ozone precursors typical for the individual cities? Can these results reflect the difference in the photochemical pollution condition and chemical environment among these cities, e.g., less serious pollution in Chongqing? A comment on this would be helpful.

Answer:

We compared the measurement presented in this study to the observation obtained by the environmental monitor stations. The Chinese EPA station data of the same year are derived. We added figures of the EPA station results in four cities in the supplement (Fig. S5). In general, the O_3 concentrations presented in this study are comparable to the maximum of monthly averaged O3 concentrations derived from the EPA monitor station data for the same year. As shown in Fig. S5, the O_3 concentrations are in general lower in Chongqing than those observed in the other three cities.

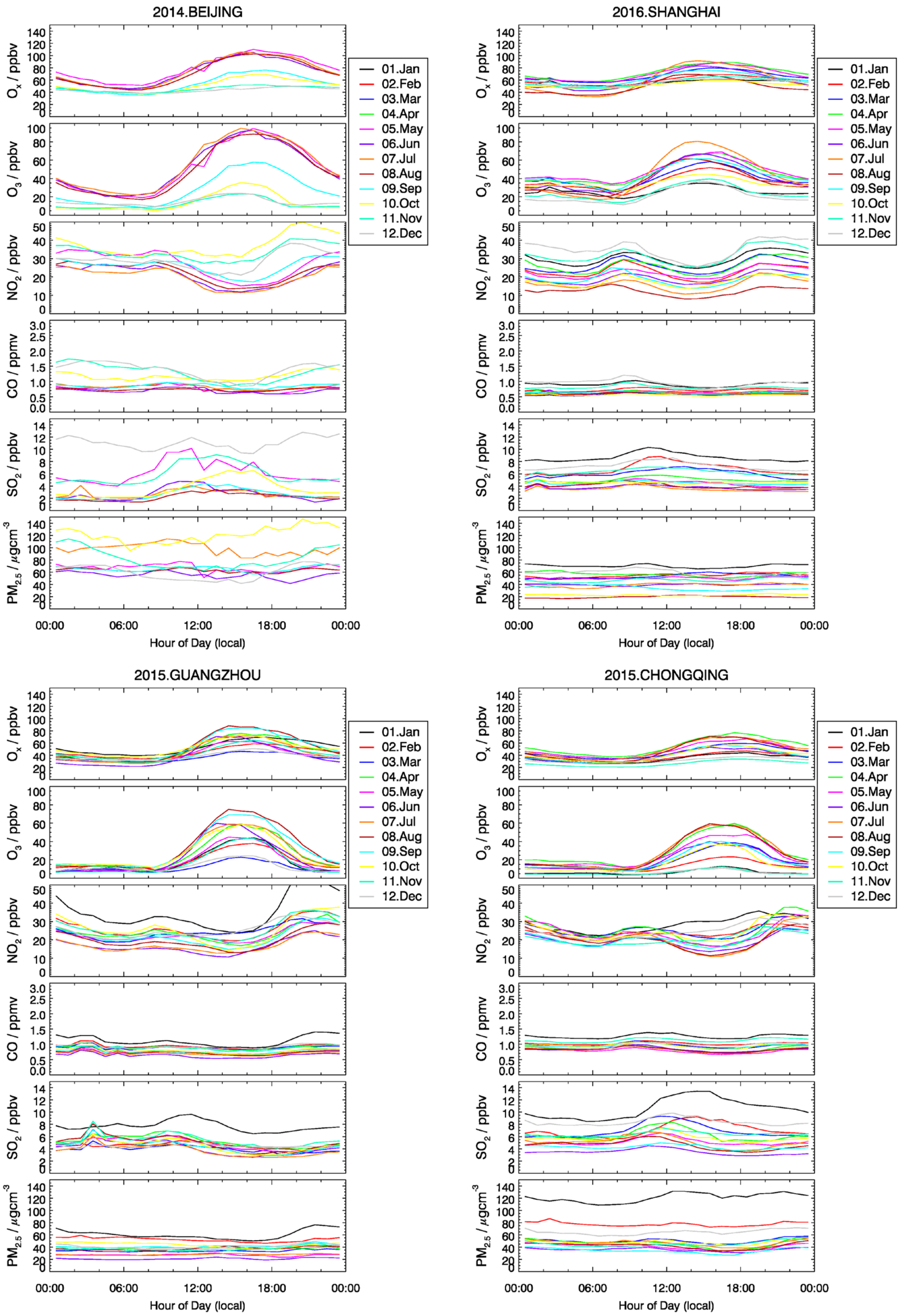

Figure S5. The monthly averaged diurnal profiles of measured O_x, O_3, NO_2, CO, PM2.5 concentrations in (a) Beijing, (b) Shanghai, (c) Guangzhou, and (d) Chongqing.

We added sentences in Line 12 Page 5 “Given the relatively short periods for these campaigns, one concern is about the representativeness of measurements. We compared the observation from these intensive campaigns to the routine measurement obtained in the environmental monitor stations operated by the Chinese environmental protection agency (Fig. S5). We found that the mean diurnal profiles of O_3 and O_x obtained in all sites are comparable to the highest monthly averaged diurnal profiles for the same city (bias < 20%). The relatively small O_3 and O_x concentrations observed in Chongqing compared to other cities (Fig. 2) is consistent with the environmental monitor stations observation (Fig. S5). Therefore, it suggests that the ozone pollution is less severe in Chongqing compared to the megacities in eastern China."

*Another concern is on the lack of direct measurements of some key radical precursors, such as HONO and carbonyls. This would influence the modeling results of radical budget as well as ozone and nitrate formation. In this study, the authors scaled the HONO concentrations to 0.02*NO2, and performed sensitivity run by turning off the scaling. But the key question here is if the scaling factor of 0.02 is appropriate. What are the scaled HONO levels in the model for the four cities? Using a different scale factor may change the budget of primary ROx sources and OH levels. The authors are recommended to perform more sensitivity tests with different scale factors and comment on its influence on the major conclusions of this study.*

Answer:

Although the HONO to NO_2 ratio is relative robust and constant as reported in other field campaigns (Elshorbany et al., 2012), such simple parameterization could increase the uncertainty of our model calculation. We performed more sensitivity tests to demonstrate the uncertainty for this simple parameterization and found the model results are not so sensitive to the parameterization (Fig. S8). We added a discussion in Line 9 Page 5 "Although the HONO to NO_2 ratio is relative robust and constant as reported in other field campaigns (Elshorbany et al., 2012), such simple parameterization could increase the uncertainty of our model calculation. To further investigate the uncertainty from this simple parameterization, the scaling factor is varied from 0.015 to 0.03. The modelled OH concentrations change by less than 10 % if the HONO scaling factors change by 50% (Fig. S8). Besides, the modelled HO_2 and RO_2 concentrations are relatively stable with different HONO scaling factors. The different scaling factors also have impact on the model generated species, e.g. HCHO (Table S4). In fact, the higher HONO concentrations lead to more active photochemical reactions and more HCHO production. The higher HCHO concentrations could further enhance the photochemistry by more radical photolytic sources in return. Therefore, the higher (lower) modelled radical concentrations due to increase (reduce) the HONO scaling factors are also affected by the corresponding change in modelled HCHO concentrations. This demonstrates the nonlinearity of the photochemical system. Nevertheless, the parameterized HONO concentrations are in the range of 0.3 to 0.6 ppbv during daytime (Table S4), which are consistent with previous in-situ measurements in urban areas (Lu et al., 2013;Li et al., 2010;Ren et al., 2003;Kanaya et al., 2007). To evaluate the impact of missing HONO source on the radical chemistry, we switched off the scaling between HONO and NO_x in a sensitivity test (Fig. S8). Therefore, the results show that OH concentrations reduce by about 20% if the only homogenous source is considered. The modeled HO_2 and RO_2 concentrations are also reduced by 15-20% (Table S4)."

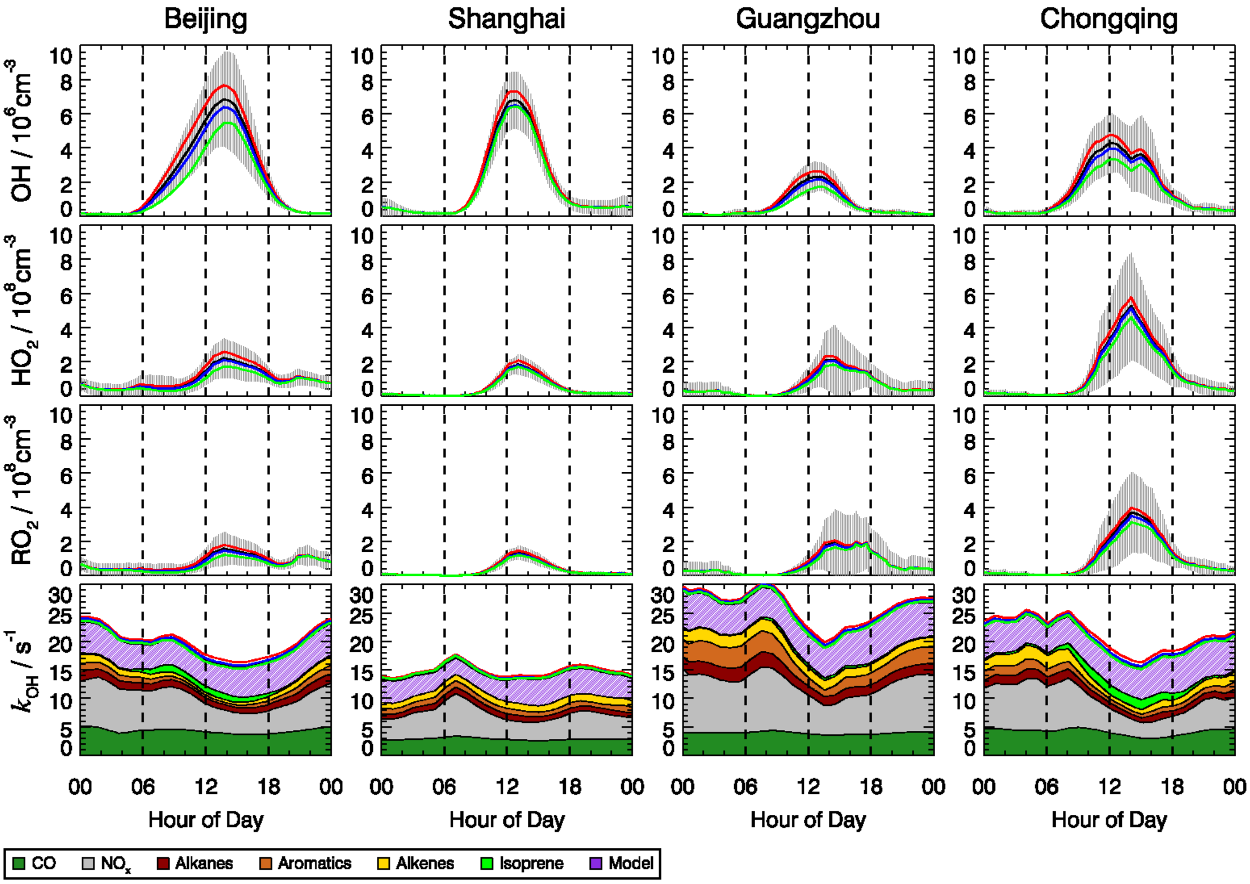

Figure S8. Mean diurnal profiles of modeled OH, HO2, RO2 concentrations and kOH in four measurement sites. Black: model base case (HONO=0.02*NO_2); Red: model sensitivity test M1 (HONO=0.03*NO_2); Blue: model sensitivity test M2 (HONO=0.015*NO_2); Green: model sensitivity test M3 (HONO unscaled but simulated free by the box model).

Moreover, how are the carbonyls treated within the model? What are the measured or simulated levels of major carbonyls such as formaldehyde, etc.?

Answer:

We added the discussion on the OVOC in Line 34 Page 8 "The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations are in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012;Song et al., 2018;Chen et al., 2016;Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation."

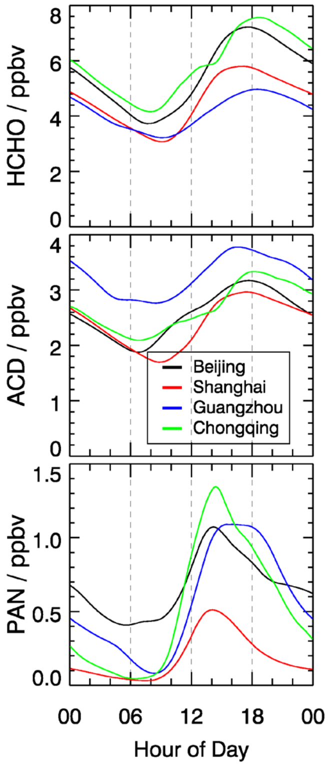

Figure S7. The mean diurnal profiles of modelled formaldehyde (HCHO), acetaldehyde (ACD) and peroxyacetyl nitrate (PAN) concentrations in four cities.

Section 3.1: a detailed discussion on the concentrations and speciation of VOCs in the four cities are needed. It is much helpful for the readers to understand the different chemical mix in these cities and to better judge the following modeling results. A table summarizing the measured VOC species and related parameters would be good.

Answer:

We added a table showing top 10 k_{OH} contributing VOCs in Table 2 and a table showing all measured VOC and their concentrations in supplement (Table S3). The mean diurnal profiles of top 10 VOC are added in supplement (Figure S6).

Table S3 Summary of measured and modelled species

Species	Parameters
Measured	T, P, RH, photolysis rate, NO, NO_2, O_3, C2-C8 alkanes, C2-C6 alkenes, C6-C10 aromatics
Modelled	OH, HO_2, RO_2, k_{OH}, OVOCs (including formaldehyde, acetaldehyde, methacrolein, other aldydes, glyoxal , acetones, methyl vinyl ketone, other ketones, methanol, ethanol, phenol, formic acid, acetic acid and higher acids, and so on)
Scaled	HONO (=0.02×NO_2)

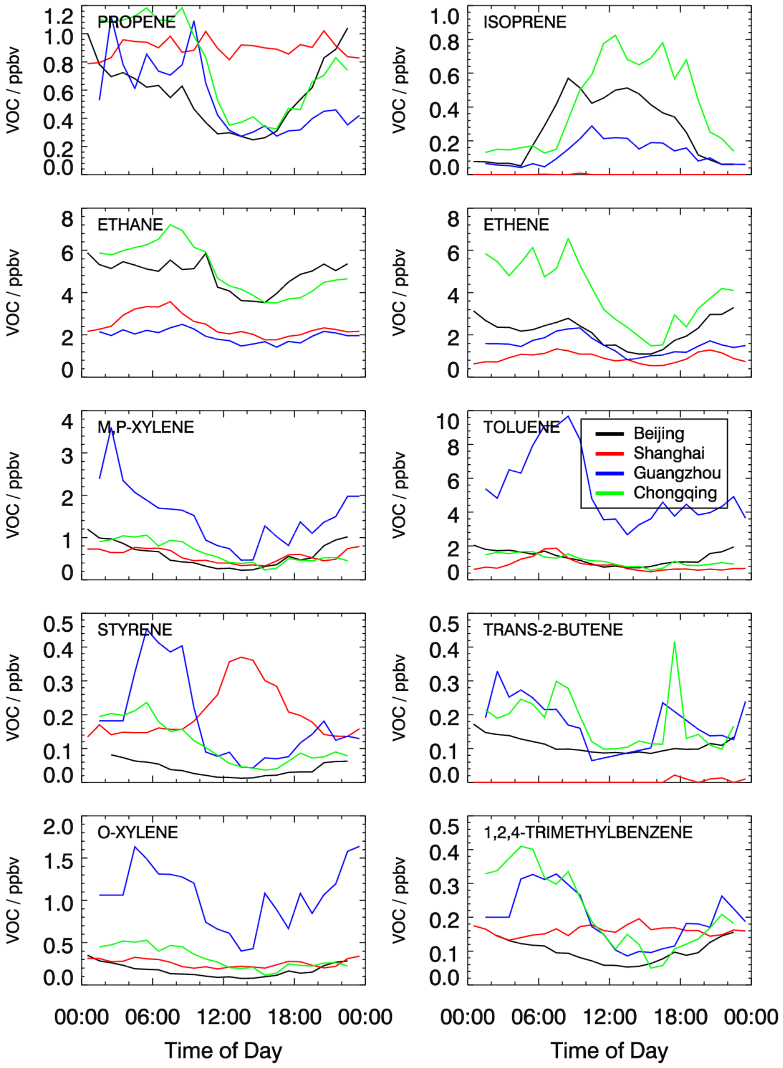

Figure S6. The mean diurnal profiles of top 10 k_{OH} contributing VOCs concentrations in Beijing, Shanghai, Guangzhou, and Chongqing.

We move the discussion of VOC speciation to section 4.1. We added a discussion on the concentrations and speciation of VOCs in the four cities in the end of the section “The top 10 OH reactivity contributing VOCs are summarized in Table 2. The order of VOCs is sorted by the averaged OH reactivity for four cities. Among all, propene are the most important OH reactivity contributor, which contributed about

0.4~0.6 s^{-1} (Table 2). The small VOCs (propene, ethane, ethene) are relatively important with respect to OH reactivity. 9 out of the top 10 VOCs are alkenes and aromatics (except ethane). In Guangzhou, the xylene (m,p-, and o-) and toluene are also important OH reactants, consistent with the inventory study (Zheng et al., 2009). The diurnal profiles are shown in Fig. S6. The observed anthropogenic VOC concentrations show typical diurnal profile that increase during night and decrease during afternoon. One exception is Shanghai site, the mean diurnal profiles of propene and 1,2,4-trimethybenzene are flat, while that of styrene shows peak around noontime, indicating unique VOC emission feature in that site.

The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations are in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012;Song et al., 2018;Chen et al., 2016;Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation. ".

Section 3.3.2 and Figures 7-8: it is interesting that ozonolysis reaction of VOCs is identified as a significant daytime source of ROx radicals in four cities. This source is usually considered to be not important at daytime as it only occurs for unsaturated VOCs which are generally at low concentration levels at daytime. So what are the major VOC species contributing to this radical source, and what are their concentration levels in these four cities? In addition, some studies found ***photolysis of OVOCs*** *is an important radical source. However, its contributions estimated in this study were quite small (3-6%) in all four cities, and the production rates of RO2 radicals (P(RO2); 0.2-0.3 ppb/h) were also much smaller compared to the other studies. These results are a little bit strange, and the authors may need examine what OVOC species are considered in the model. More discussions of the radical budget analysis are needed.*

Answer:

As shown in the newly added Table 2, 5 out of the top 10 VOC could react with O_3 to produce ROx radicals. However, the reaction rates with O_3 and with OH are different for different alkenes. We added a discussion in Line 17 Page 9 "The ozonolysis reactions mainly contributed by trans-2-butene in Beijing (55%), Guangzhou (42%), and Chongqing (39%), whose concentrations are in the range between 0.1 to 0.3 ppbv (Fig. S6). Although trans-2-butene is only the 8th important VOCs with respect to OH reaction (Table 2), it become the most important O_3 reactants producing RO_x radicals due to its fast reaction rate with O_3 (1.9×10^{-16} $cm^{-3}s^{-1}$ compared to 1.0×10^{-17} $cm^{-3}s^{-1}$ of propene, rate constant derived from MCM3.3.1 (http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt)). In Shanghai, propene becomes the most important alkene with respect to O_3 reaction, which accounts for about 42% of the total alkene ozonolysis reactions. Actually, the relatively high contribution from alkene ozonolysis to the RO_x radical primary sources could be one of the important characteristics for RO_x radical primary sources in Chinese megacity. The importance of alkene ozonolysis was also found in Santiago, Chile (Elshorbany et al., 2009) and Essex, UK (Emmerson et al., 2007), where alkene ozonolysis contributed about 20% to the total radical primary production."

The role of OVOCs (except HCHO) photolysis are highly variable from literatures, which demonstrates the fate OVOCs highly depends on chemical conditions. We added a discussion on the role of OVOC photolysis to radical chemistry from Line 30 Page 10 to Line 2 Page 11 to replace the sentences "The RO_2 primary source strength is in the range of 0.2 to 0.3 ppbv/h, which is mainly contributed by alkene ozonolysis and OVOC photolysis (Fig. 8). In this study, the OVOC photolysis mainly includes carbonyl-containing compounds (e.g. acetaldehyde, aldehydes with carbon numbers larger than 3), which are generated by the box model. The modelled acetaldehyde concentrations are in the range of 2 to 4 ppbv (Fig. S7), consistent to the observations in Beijing (Chen et al., 2016) and Hong Kong (Lyu et al., 2016). The photolysis rate of carbonyl-containing compounds (except HCHO) is about one third to a quarter of the HCHO photolysis rate. In comparison, this ratio could be close to or even higher than 1 in other urban studies (Ren et al., 2013;Volkamer et al., 2010;Emmerson et al., 2007;Michoud et al., 2012;Whalley et al., 2018;Xue et al., 2016). In contrast, the relatively small contribution from other carbonyl-containing compounds photolysis than HCHO photolysis were reported in an urban and suburban site in Hong Kong (Lyu et al., 2016), where the acetaldehyde concentrations were about 1 to 2 ppbv, comparable to our model simulation. Such large discrepancy in the role of other OVOC photolysis to the radical production highlights the importance to measure these radical precursors in the future studies."

Specific Comments:

Title: Atmospheric oxidation capacity in four Chinese megacities

Answer:

We changed the title to be "Daytime atmospheric oxidation capacity in four Chinese megacities during photochemical polluted season: a case study based on box model simulation".

Page 1, Line 40: is one of the major threats

Answer:

Corrected.

P2, L1-2: it would be better to introduce Chongqing here after introducing the other three megacities

Answer:

We moved the introduction of Chongqing to Line 6 Page 2 “The Chengdu-Chongqing city group (population 90 million) locates in Sichuan Basin (SCB), southwest of China, representing the developing city clusters. Chongqing is the biggest city in the southwest of China, which suffers from severe air pollution as well.”
We moved the sentence “Although the new city clusters also suffer from air pollution, only sparse researches have been conducted in these regions, especially for the secondary pollution formation. For the SCB region, only limited studies have been performed regarding the oxidation capacity. Chengdu is evaluated using an observational-based model which found similar radical concentration and ozone production rate (Tan et al., 2018c). The VOC and ozone formation is evaluated in Chongqing (Su et al., 2018;Li et al., 2018b).” to Line 37 Page 2.

P2, L4: have declined characterized by high concentrations of ozone and fine particles

Answer:

We changed the sentence to be “As a result, the primary pollutant concentrations have declined since then. However, secondary pollution characterized by high concentrations of ozone and fine particle has become the major contributor to air pollution.”

P2, L11: the role of

Answer:

Corrected.

P3, L7: are located

Answer:

Corrected.

P3, L16: according to Table 1, the measurement in Beijing was in July, not in June.

Answer:

Corrected.

P3, L21: Instrumentation

Answer:

Corrected.

Section 2.2: a table summarizing all of the measurement species (especially the VOC species) and techniques is needed, maybe in the supplement, for better understanding the present study.

Answer:

We added a table to describe the instrumentation in the supplement (Table S1). The measured VOCs listed are presented in Table S3.

P3, L29-30: rephrase this sentence.

Answer:

We changed the sentence to be “A box model based on the Regional Atmospheric Chemical Mechanism version 2 (Goliff et al., 2013) is used to simulate the concentrations of the OH, HO_2 and RO_2 radicals concentrations and other unmeasured secondary species concentrations.”

P4, L5: AHC is used here but AVOCs is used later. Keep them consistent and spell out them at their first appearance.

Answer:

We changed all AHC to AVOC. For consistency, we changed NHC to NVOC.

P5, L1-8: it seems that the discussion in this paragraph is not relevant here

Answer:

We rearrange the paragraph from Line 34 Page 5 to Line 10 Page 6.

P6, L4-5, “The maximum of OH”: rephrase this sentence.

Answer:

We changed the sentence to be “The peak of OH mean diurnal profile is highest in Beijing and Shanghai (7×10^6 cm^{-3}).”

P6, L13-14, “the larger correlation slope”: rephrase this sentence since solar radiation cannot directly converts to radicals

Answer:

This sentence is only a qualitative description and not related to the content. Hence, we removed this sentence.

P9, L33-34: a brief discussion of the NHC levels would be much helpful here.

Answer:

We added a sentence in Line 15 Page 13 “The only component of NVOC is isoprene, which are on average 0.3 ppbv in Beijing, 0.1 ppbv in Guangzhou, and 0.4 ppbv in Chongqing, but reduce to negligible in Shanghai (below detection limit, Table S3).”

P9, L35-36: "reducing NOx could lead to increase in Ox concentrations" is not absolutely correct. There is a threshold below which the NOx emissions were reduced to, the ozone would be significantly decreased.

Answer:

We changed the sentence to be "For NO_x, the RIR values are negative indicating the ozone production is in NO_x-titration regime. A slight reduction of NO_x could lead to increase in O_x concentrations within the NO_x-titration regime."

P10, L6, "In another word, if HONO is": uncomplete sentence.

Answer:

The sentence should be "The reduction of radical termination by $OH+NO_2$ reaction compensates the reduction of radical primary source due to HONO photolysis. Therefore, a larger negative effect shows up in the RIR analysis in the sensitivity test (Fig. S6)."

P10, L34: change decomposition to deposition

Answer:

Changed.

Section 4.2: is the nocturnal nitrate formation from the N2O5-related processes taken into account in the present analysis?

Answer:

Only daytime processes is considered in this study. I added a sentence to state it in Line 1 Page 15 "One should note that the nitration formation from N_2O_5 hydrolysis is not taken into account in this study, which could lead to negative bias in the nitrate production."

P12, L25: change Shang to Shanghai

Answer:

Corrected.

Figure 2: Anthropogenic Volatile Organic Compounds (AHC): keep consistent.

Answer:

We changed all AHC to AVOC.

Figure 3: Chengdu should be Chongqing? In addition, what does "model" mean in the figure legend?

Answer:

We changed the caption to be "Figure 3. Mean diurnal profile of contributions from all measured species for OH reactivity in Beijing, Shanghai, Guangzhou, and Chongqing. The filled areas represent different atmospheric constituents. The model denotes the sum of model generated species such as formaldehyde, acetaldehyde."

Figure 6: what does "variability" stand for?

Answer:

We changed the caption to be "The vertical bars denote the daily variability of model calculated radical concentrations."

Anonymous Referee #2

Received and published: 17 December 2018

This manuscript describes constrained photochemical modeling of four large urban areas in China. The paper is difficult to read due to organization, presentation and grammar. I found it difficult to understand what exactly was modeled or measured and how. The conclusion that all four cities are VOC limited is probably correct and probably worth noting for these cities. However, some of the conclusions such as the importance of some radical sources is more difficult to justify as they are not based on observations. I have included major and minor comments below. However, please note the manuscript needs significant editing for style and grammar beyond my suggestions. I think this paper is only publishable after major revisions.

Answer:

We thank the comments and suggestions from the reviewers, which help to improve the manuscript considerably. The response and changes are listed below. We also changed the style and grammar of the paper and please find them in the revised manuscript.

1) The title and abstract indicate that the "atmospheric oxidation capacity" is the focus of the paper. That is fine but this term should be defined instead of vaguely described as in the first line of the abstract. Once defined the values for the different cities should be reported – preferably in the abstract and in the results. I would define the AOC as the reactions of OH, ozone, NO3, etc. that lead to oxidation of an atmospheric component. I would expect units of something like the amount of oxidized molecules per time. The authors only include OH in their reporting of AOC and only vaguely report the values. This needs to be tightened up. I am sure that OH dominates but ozone and NO3 may be important at night and this should needs to be at least mentioned.

Answer:

In the revised manuscript, we restrict the oxidation capacity to daytime photochemical reaction. Also, we point out the focus of this study will be mainly on OH radical chemistry. We changed the title to be "Daytime atmospheric oxidation capacity in four Chinese megacities during photochemical polluted season: a case study based on box model simulation".

In the beginning of the abstract, we changed the Line 25-26 Page 1 "Atmospheric oxidation capacity AOC is the core of converting freshly-emitted substances to secondary products, which are dominated by reaction with hydroxyl radicals (OH) during daytime." We added a sentence to define AOC and restrict it to OH oxidation only in Line 9 Page 3 "AOC can be defined as the sum of respective oxidation rates of trace gases (VOCs, CO, and NO_x) by the oxidants (OH, O_3, and NO_3) (Geyer et al., 2001). Given the relatively importance of OH oxidation during daytime, the AOC is restricted to OH oxidation in this study."

2) When I read the abstract, I thought this was going to be more of an observational study than a modeling project. I expected to see observations of OH, HO2, etc. So I recommend stating clearly that this is a photochemical modeling study constrained by observations of NOx, ozone, etc. For example, I initially thought that OH reactivity was measured in this study instead of being calculated from VOC observations. So please make it clear what is measured and how. The lack of any detail in the instrumentation section is unacceptable in my opinion. I suggest that a table be made of every parameter that is measured, including the method, and a reference. I realize standard commercial instruments perform some of the measurements such as ozone and CO. However, many of the measurements are not run of the mill. In particular, there needs to be a reference to the VOC measurement method and a list of measured compounds and detection limits listed in the supporting information.

Answer:

As mention previously, we changed the title to be more explicitly demonstrating this is a model-based study. We added a table to describe the instrumentation in the supplement (Table S1). We added a sentence in Line 8 Page 4 “The performance of different instruments is summarized in Table S1.”

Table S1 measured species for ozone pollution analysis and instrument time resolution, accuracy and limit of detection

Species	Method	Time resolution	Accuracy (1σ)	Limit of Detection / ppbv
Photolysis frequencies	Actinic flux spectroradiometry	20 s	±10 %	Five orders of magnitude lower than maximum at noon
O_3	UV absorption	1 min	5%	0.5
NO	Chemiluminescence	1 min	±20 %	60 pptv
NO_2	Chemiluminescence	1 min	±20 %	0.3
CO	IR absorption	1 min	5%	4
VOCs	Gas chromatography and mass spectroscopy /flame ionization detector	1 h	10%~20%	0.01~0.2

We also prepared a table in supplement to state what are measured, modelled, and parameterized in this study (Table S2). The measured VOCs and their concentrations are presented in table S3. We added a sentence in Line 23 Page 4 “The measured, modelled and parameterized parameters are summarized in Table S3.”

We added a description about the VOC measurement in Line 9 Page 4 “VOC measurements (including 55 organic species) were performed by commercial an instrumentation using gas chromatograph (GC) equipped with a mass spectrometer (MS) and a flame ionization detector (FID). In principle, the air sample was drawn into two parallel channels for enrichment by cooling before analysis (Wang et al., 2014). The VOCs measurements include C_2–C_{11} alkanes, C_2–C_6 alkenes, and C_6–C_{10} Aromatics (Table S2).”

Table S2 Summary of measured VOCs concentration for four campaigns

	Beijing			**Shanghai**			**Guangzhou**			**Chongqing**		
VOC / ppbv	**Mean**	**Median**	**Max**	**Mean**	**Median**	**Max**	**Mean**	**Median**	**Max**	**Mean**	**Median**	**Max**
1,2,3-TRIMETHYLBENZENE	0.026	0.022	0.100	0.130	0.120	0.340	0.090	0.065	0.473	0.068	0.053	0.189
1,2,4-TRIMETHYLBENZENE	0.098	0.085	0.370	0.160	0.150	0.610	0.199	0.121	1.140	0.225	0.161	0.756
1,3,5-TRIMETHYLBENZENE	0.022	0.018	0.111	0.004	0.000	0.230	0.077	0.053	0.347	0.079	0.058	0.337
1-BUTENE	0.167	0.140	0.803	0.072	0.060	0.300	0.239	0.218	0.607	0.193	0.146	0.939
1-HEXENE	Nan	Nan	Nan	0.323	0.280	1.870	0.074	0.048	0.429	0.065	0.062	0.193
1-PENTENE	0.025	0.019	0.156	0.049	0.020	0.330	0.049	0.033	0.295	0.057	0.042	0.471
2,2,4-TRIMETHYLPENTANE	0.051	0.045	0.240	0.155	0.130	0.990	0.072	0.039	0.736	0.056	0.045	0.177
2,2-DIMETHYLBUTANE	0.020	0.019	0.070	0.149	0.140	0.410	0.099	0.063	0.898	0.054	0.037	1.236
2,3,4-TRIMETHYLPENTANE	0.021	0.019	0.094	0.023	0.000	0.350	0.045	0.028	0.336	0.026	0.022	0.071
2,3-DIMETHYLBUTANE	0.033	0.028	0.137	0.071	0.070	0.180	0.137	0.072	1.584	0.077	0.058	0.769
2,3-DIMETHYLPENTANE	0.049	0.038	0.469	0.027	0.000	0.490	0.111	0.061	0.667	0.056	0.040	0.353
2,4-DIMETHYLPENTANE	0.039	0.037	0.099	0.112	0.100	0.350	0.070	0.046	0.379	0.030	0.024	0.142
2-METHYLHEPTANE	0.016	0.014	0.050	0.002	0.000	0.210	0.066	0.046	0.440	0.039	0.032	0.162
2-METHYLHEXANE	0.061	0.055	0.227	0.000	0.000	0.000	0.273	0.174	1.391	0.133	0.095	0.976
2-METHYLPENTANE	0.226	0.206	0.983	0.265	0.230	1.610	1.066	0.557	8.730	0.360	0.268	3.827
3-METHYLHEPTANE	0.021	0.019	0.066	0.095	0.100	0.210	0.054	0.037	0.345	0.024	0.020	0.113
3-METHYLHEXANE	0.107	0.093	0.307	0.116	0.110	0.260	0.299	0.177	1.936	0.150	0.101	1.196
3-METHYLPENTANE	0.277	0.252	1.027	0.130	0.110	0.580	0.716	0.378	4.242	0.363	0.259	4.246
BENZENE	0.909	0.780	7.830	0.413	0.350	1.240	0.989	0.560	11.448	1.080	0.995	3.749
CIS-2-PENTENE	0.005	0.004	0.045	0.015	0.000	0.670	0.014	0.007	0.107	0.023	0.005	0.287
CIS-BUTENE	0.035	0.019	0.301	0.003	0.000	0.280	0.122	0.124	0.259	0.143	0.100	1.333
CYCLOHEXANE	0.079	0.058	1.048	0.097	0.080	0.320	0.222	0.103	2.180	0.079	0.064	0.293
CYCLOPENTANE	0.125	0.117	0.355	0.048	0.050	0.150	0.117	0.108	0.313	0.167	0.135	0.716
ETHANE	4.896	4.570	13.941	2.432	2.300	7.570	1.952	1.661	5.029	5.145	4.957	11.305
ETHENE	2.210	2.087	7.887	0.921	0.700	5.290	1.522	1.242	6.875	4.039	3.435	11.949
ETHYLBENZENE	0.335	0.257	1.636	0.355	0.290	1.460	1.322	0.782	16.959	0.625	0.480	2.176
ETHYNE	Nan	Nan	Nan	0.025	0.020	0.130	1.355	1.263	2.949	4.123	3.649	11.352
ISO-BUTANE	1.836	1.747	6.574	0.779	0.650	3.760	1.884	1.536	6.630	0.652	0.542	3.581
ISO-PENTANE	1.414	1.326	3.941	0.691	0.560	3.110	1.205	1.079	5.581	1.987	1.412	34.131
ISO-PROPYLBENZENE	0.011	0.010	0.056	0.033	0.000	0.940	0.047	0.037	0.230	0.032	0.026	0.096
ISOPRENE	0.272	0.208	1.289	0.000	0.000	0.110	0.126	0.088	0.809	0.404	0.332	1.641
M-DIETHYLBENZENE	Nan	Nan	Nan	0.217	0.190	0.820	0.036	0.035	0.181	0.026	0.020	0.088
M-ETHYLTOLUENE	0.052	0.045	0.206	0.033	0.000	0.500	0.168	0.122	0.779	0.150	0.111	0.666
M,P-XYLENE	0.604	0.413	3.006	0.565	0.420	3.180	1.508	0.770	24.621	0.655	0.511	2.352
METHYLCYCLOHEXANE	0.074	0.056	0.344	0.003	0.000	0.460	0.187	0.085	2.100	0.189	0.064	4.341
METHYLCYCLOPENTANE	0.121	0.107	0.399	0.064	0.050	0.190	0.296	0.161	2.022	0.120	0.088	0.776
N-BUTANE	2.579	2.403	8.366	0.770	0.600	3.360	2.790	2.339	9.093	1.050	0.847	6.242

N-DECANE	0.021	0.018	0.093	0.074	0.070	0.270	0.108	0.071	0.544	0.086	0.068	0.206
N-HEPTANE	0.116	0.095	0.386	0.037	0.000	0.310	0.197	0.113	1.420	0.209	0.158	1.230
N-HEXANE	0.232	0.170	1.271	0.414	0.260	2.960	0.975	0.480	7.397	0.469	0.318	3.201
N-NONANE	0.033	0.026	0.187	0.057	0.050	0.270	0.079	0.048	0.434	0.469	0.361	1.607
N-OCTANE	0.046	0.037	0.191	0.100	0.080	0.440	0.107	0.072	0.720	0.091	0.078	0.244
N-PENTANE	0.877	0.762	2.383	0.508	0.480	1.280	0.751	0.626	3.083	0.936	0.657	7.593
N-PROPYLBENZENE	0.023	0.021	0.074	0.065	0.060	0.210	0.067	0.057	0.210	0.059	0.051	0.201
N-UNDECANE	0.033	0.030	0.136	0.011	0.000	0.190	0.094	0.073	0.396	0.133	0.115	0.291
O-ETHYLTOLUENE	0.024	0.021	0.086	0.058	0.050	0.200	0.078	0.057	0.322	0.067	0.055	0.263
O-XYLENE	0.175	0.126	0.933	0.256	0.200	1.270	1.058	0.633	8.043	0.327	0.256	1.176
P-DIETHYLBENZENE	Nan	Nan	Nan	0.000	0.000	0.000	0.071	0.050	0.563	0.054	0.042	0.151
P-ETHYLTOLUENE	0.030	0.025	0.127	0.043	0.040	0.160	0.107	0.076	0.478	0.086	0.070	0.329
PROPANE	3.651	3.456	11.666	2.355	2.130	9.360	4.801	3.754	20.957	1.221	1.121	2.860
PROPENE	0.581	0.496	2.472	0.897	0.870	3.430	0.568	0.358	3.387	0.785	0.717	2.336
STYRENE	0.040	0.026	0.383	0.202	0.170	1.270	0.180	0.079	2.078	0.119	0.084	0.493
TOLUENE	1.319	1.055	6.400	0.867	0.550	5.290	5.312	3.041	39.897	1.154	0.963	3.594
TRANS-2-BUTENE	0.110	0.092	0.470	0.003	0.000	0.260	0.201	0.186	0.395	0.175	0.125	1.851
TRANS-2-PENTENE	0.008	0.003	0.136	0.024	0.000	0.860	0.026	0.011	0.355	0.052	0.008	0.771

In addition, I do not know what NO2 chemical conversion to NO means as stated on line 25 of page 3. This needs to be described and the probability of interference from PAN needs to be discussed. I would expect at least 5 ppbv of PAN in areas such as Beijing during the day. This could lead to a significant interference in NO2. Please also report in more detail on the VOC observations. I think at least averages of the top 10 or 5 VOC in terms of OH loss should be listed for each city. I like the graphs in the supplement but the scales on many of the graphs don't make sense. Often the parameter graphed only goes up to 10 or 20% of full scale making it impossible to see what is going on. I don't think keeping consistent axes between different cities is worth not being able to read the graph.

Answer:

We changed the sentence to be "… after chemical conversion to NO." to be "in the form of NO by chemical conversion using Molybdenum convertor. This conversion method is known to be interference by NO$_z$ species, which could be converted to NO. Therefore, one should keep in mind that the NO$_2$ measurement presented in this study could be positive biased from the ambient NO$_2$ concentrations." Besides, we derived the PAN concentrations from our box model calculations, which are about 2 ppbv (Fig. S7).

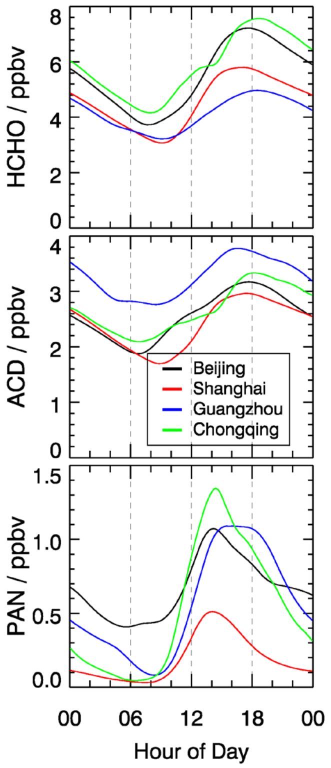

Figure S7. The mean diurnal profiles of modelled formaldehyde (HCHO), acetaldehyde (ACD) and peroxyacetyl nitrate (PAN) concentrations in four cities.

We added a table about measured VOC in supplement (Table S3) and a table showing top 10 k_{OH} contributing VOCs (Table 2). The mean diurnal profiles of top 10 VOCs are added in supplement (Fig. S6). A detail discussion on the measured VOCs is added. Please find the answers in the response to referee #1 who has the similar comments.

We changed the scale of the Fig. S1-S4 as suggested (see below).

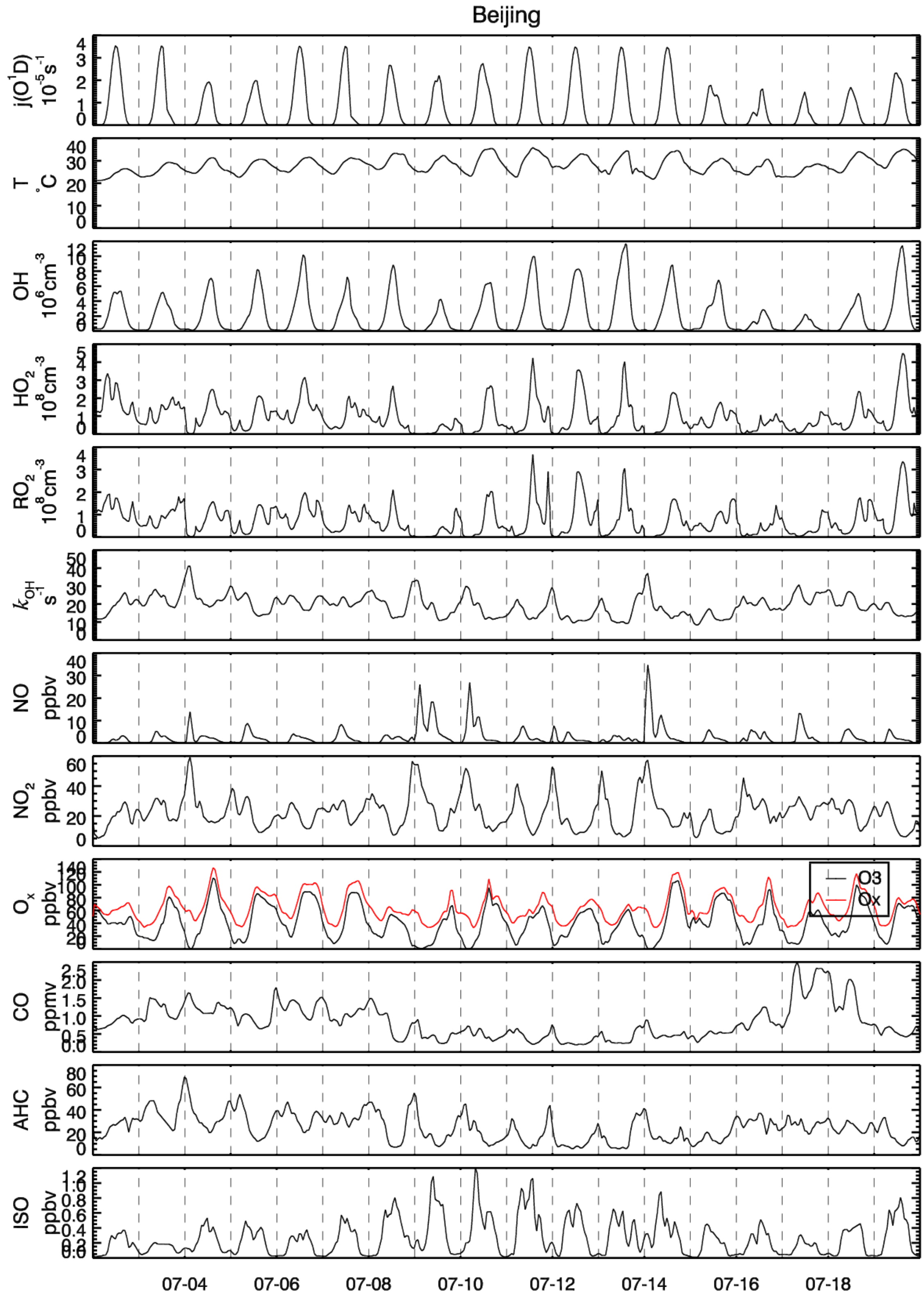

Figure S1 The time series of measured parameters (j(O^1D), Temperature, NO, NO_2, O_3, O_x, CO, AHC, isoprene) and modelled OH, HO_2, and RO_2 concentrations and OH reactivity in Beijing.

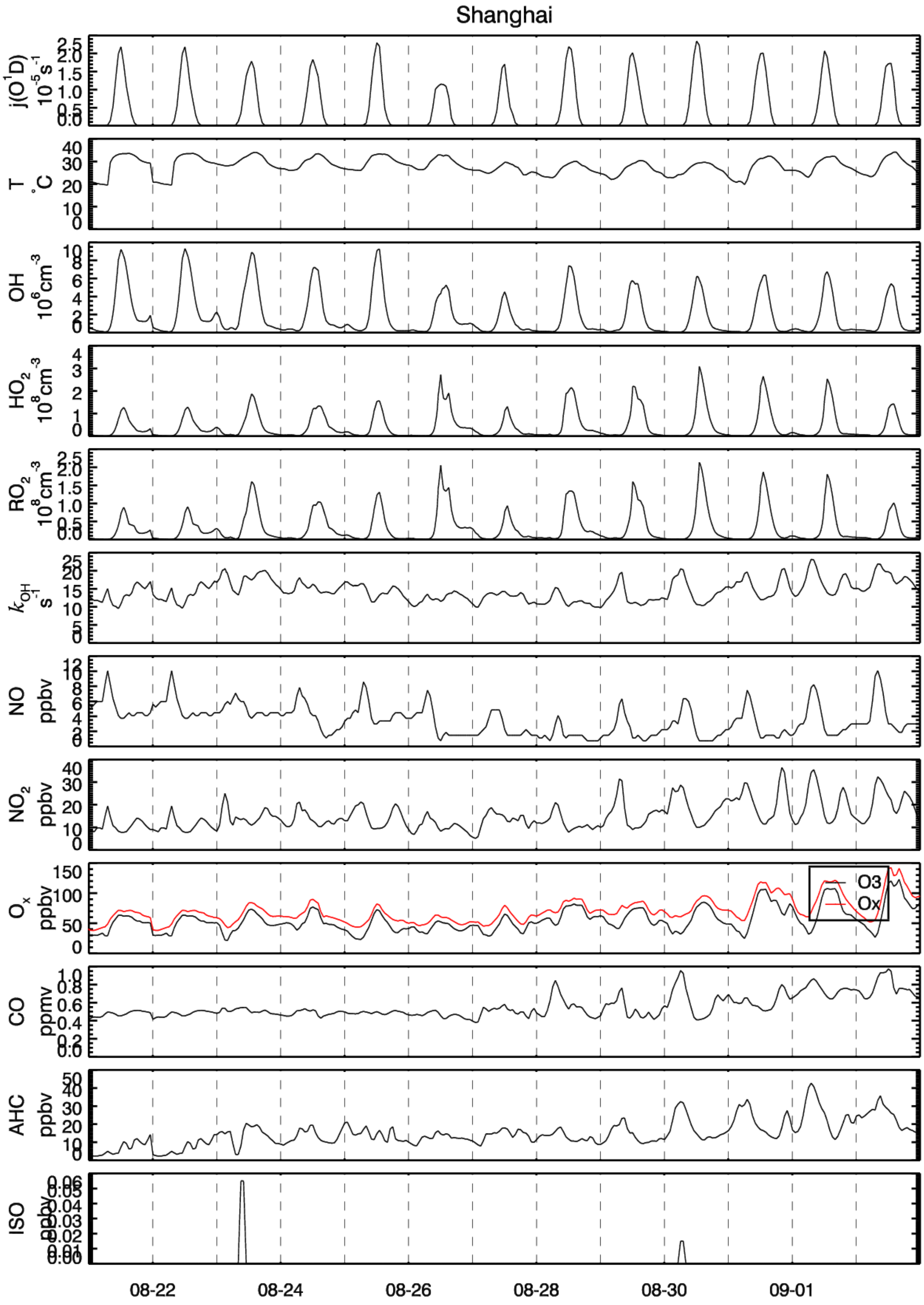

Figure S2 The time series of measured parameters (j(O^1D), Temperature, NO, NO_2, O_3, O_x, CO, AHC, isoprene) and modelled OH, HO_2, and RO_2 concentrations and OH reactivity in Shanghai.

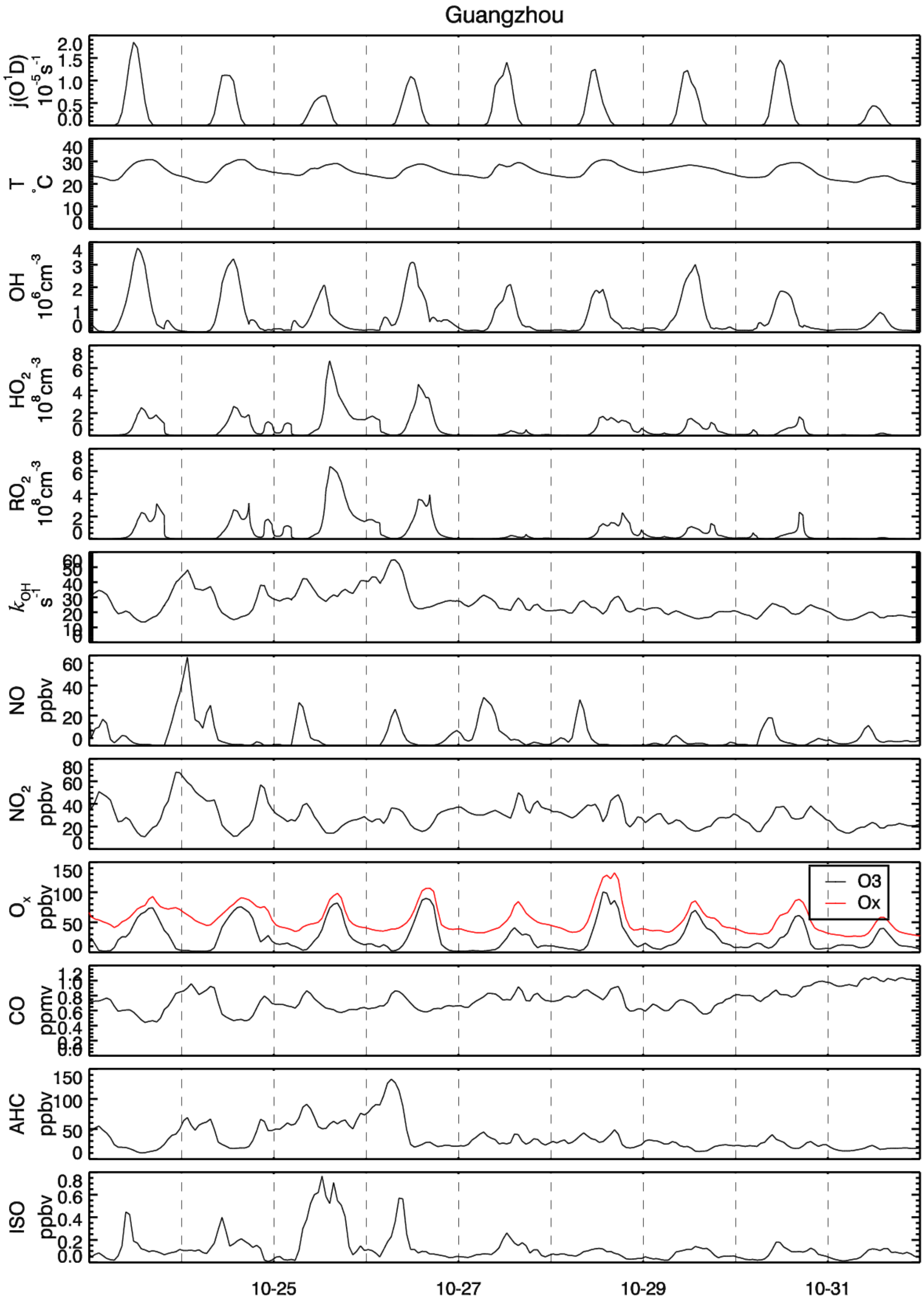

Figure S3 The time series of measured parameters (j(O^{1}D), Temperature, NO, NO$_2$, O$_3$, O$_x$, CO, AHC, isoprene) and modelled OH, HO$_2$, and RO$_2$ concentrations and OH reactivity in Guangzhou.

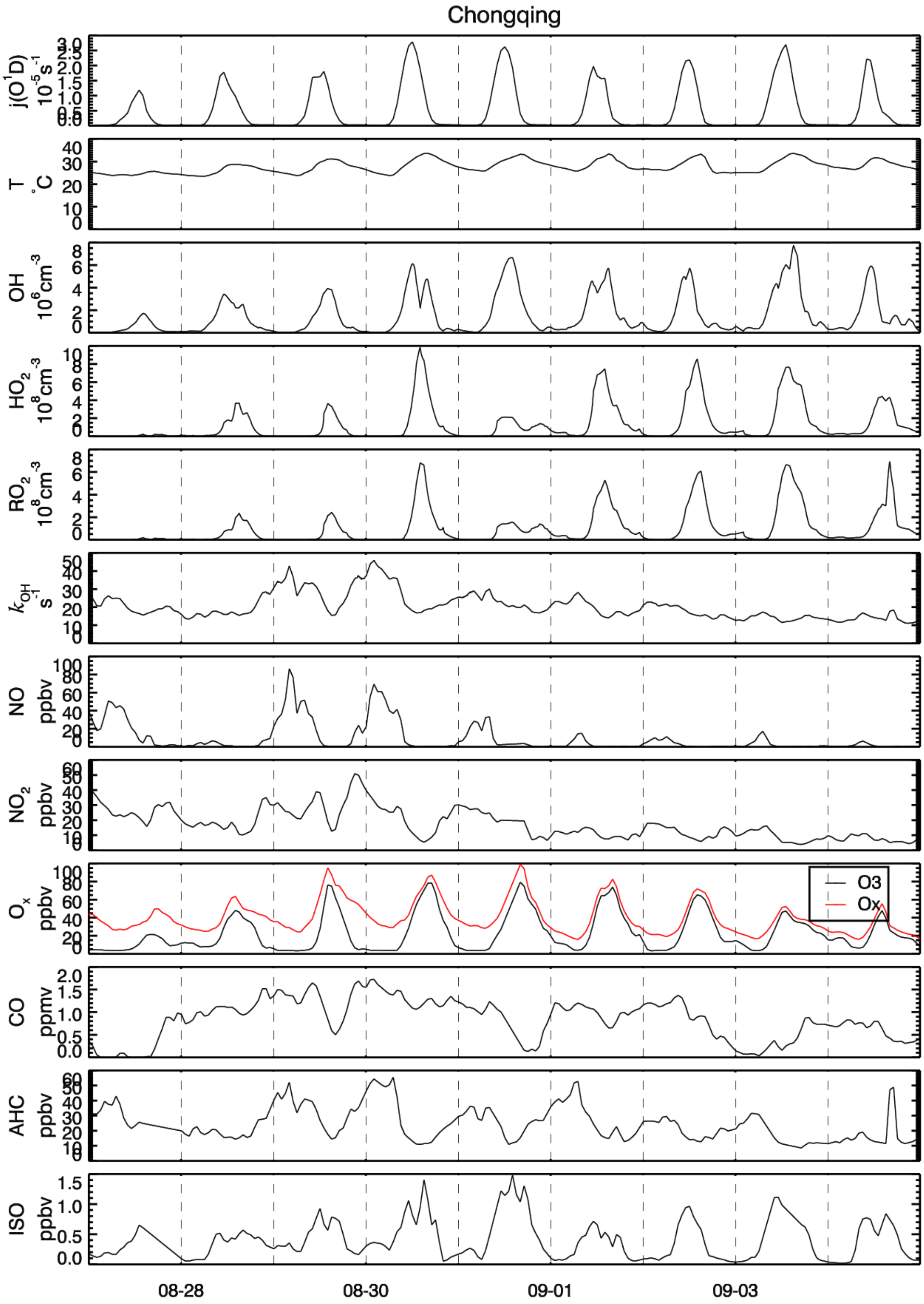

Figure S4 The time series of measured parameters (j(O^{1}D), Temperature, NO, NO$_2$, O$_3$, O$_x$, CO, AHC, isoprene) and modelled OH, HO$_2$, and RO$_2$ concentrations and OH reactivity in Chongqing.

3) The reporting of OH reactivity could be made much simpler as well. Perhaps having a section in the results showing the VOC observations separately would be less confusing. You could then have a following section on the calculated OH reactivity. I really recommend limiting the discussion in these sections and focusing on the results. For example, the paragraph on line 1 page 5 stating that OH reactivity can be measured in 3 ways made me think for some time that this was a measured quantity in this work.

Answer:

We removed the part of the description of OH reactivity measurement techniques. The description of VOC measurement and discussion are moved to section 4.1. Please see detail in the response to referee#1.

4) I highly recommend being more explicit on what is derived from the model or parameterized. For example, I don't think formaldehyde or acetaldehyde are measured but are model predicted. If so this needs to be described and predicted levels compared to observations if available. This will certainly impact the radical budget as well as the production rate of PAN relative to HNO3. So I suggest a table of model parameters that are predicted, constrained, and parameterized. I also suggest that the model results be presented in an organized manner in the results section. There is a lot of discussion throughout section 3 that should probably be in section 4.

Answer:

Similar to the comments (2), we prepared the table in supplement to state what are measured, modelled, and parameterized in this study (Table S2). We added a sentence in the new section 4.1 to discuss the modeled OVOC concentration "The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations were in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012;Song et al., 2018;Chen et al., 2016;Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but on average 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation."

We restructured the manuscript by moving the VOC description to section 4.1 and moving the OH-HO_2-RO_2 budget analysis (originally section 3.3.2) to section 4.2.

5) The very simple parameterization of HONO as being 2% of NO2 is somewhat troubling. I am surprised that it would be that simple especially as a function of the time of day. I think this assumption needs to be better justified and probably looked at to determine the sensitivity, i.e. some case studies with different assumptions are probably needed. This is also another reason to describe the NO2 measurement in more detail.

Answer:

Referee #1 has similar concern on the uncertainty in HONO parameterization. We performed more sensitivity study to investigate the uncertainty and please find our answer in the response to Referee#1.

6) I am not sure the ISOROPPIA modeling adds much to the paper especially as there are no measurements of ammonia or nitric acid. I certainly realize that if there is a large excess of ammonia that this will drive nitric acid into the aerosol. However, I am not sure the nitric formation rate vs. loss rate to aerosol versus dry and wet deposition can be suitably treated in this work to allow for quantitative predictions of ammonium nitrate aerosol. So I recommend removing from the paper and perhaps replacing with a simple discussion. This discussion could also mention that cutting down NOx may lead to enhanced ozone production but it will cut down on particulate nitrate as well.

Answer:

We agree that the calculation may not be quantitative since some key parameters, e.g. ammonia and nitric acid concentrations were not measured during these campaigns. We reduce the content in the section Nitrate production potential. We also moved some of the contents and original Table 2 to supplement. Please find the changes in the main text following.

“Nitric acid is one of the major products generated by the radical system for high NO_x conditions, which is an important precursor of particulate nitrate (NO_3^-). Recently, nitrate has become a significant portion in particles in Beijing, Shanghai, and Nanjing (YRD) during summertime in China (Li et al., 2018a). The gas phase nitric acid HNO_3 together with ammonium NH_3 form a gas-particle partitioning equilibrium with NH_4NO_3 (R3), which depends on the relative humidity, temperature, and the aerosol contents (Seinfeld and Pandis, 2016).

$$\mathrm{NH_3} + HNO_3 \leftrightarrow NH_4NO_3 \qquad \text{(R3)}$$

The nitric acid is mainly produced from the reaction between NO and OH which can be derived from the box model. The fate of nitric acid depends on the gas-particle partition, deposition and chemical reactions. In general, the time scale of partitioning is 1-2 orders smaller than those of deposition and chemical production (Morino et al., 2006;Neuman et al., 2003). Therefore, the photochemical produced nitric acid will deposit on to the aerosol if the ambient NH_3 is sufficient. The deposition rate is about 7 cm s^{-1} (Seinfeld and Pandis, 2016), which results in a deposition timescale being 8 hours if the boundary layer height is 2 km (typical values for summertime). The ammonia concentrations are usually above 10 μg/m^3 in urban areas in China during summertime (Pan et al., 2018), which indicates ammonia-rich conditions and sufficient to neutralize nitric acid..

In this study, we use the aerosol thermodynamic model (ISORROPIA) to simulate the nitrate production and the model design is explained in supplement. It’s worth noting that such model simulation cannot be quantitatively because some key parameters, e.g. ammonia and nitric acid concentrations were not measured during these campaigns. The discussion below should be considered as a qualitative estimation to show the important feature in determining the particle nitrate production. The modeled nitrate concentration and partitioning in Beijing are shown to illustrate the typical pattern of particulate nitrate formation (Fig. 11a). The total nitrate concentrations maximize in the late afternoon while the particulate nitrate shows a board peak at night, which is mainly driven by the stronger gas-to-particle partitioning due to higher RH. Since deliquesce relative humidity (DRH) of NH_4NO_3 is about 60% in all cases, the partitioning changed dramatically with the relative humidity above DRH (nighttime) and below DRH (daytime). One should note that the nitrate formation from N_2O_5 hydrolysis is not taken into account in this study, which could lead to negative bias in the nitrate production calculation.

To investigate the nitrate concentration dependence on the nitrate production rate and ambient ammonia concentrations, the averaged nitrate concentrations are plotted as a function of daily integrated nitric acid production rate and total ammonium ($NH_4^+{}_{(a)}$+$NH_{3(g)}$) concentrations. As shown in Fig. 11b, the isopleth diagrams are split into two parts by the dashed line to represent the nitrate- (upper left) and ammonium-sensitive (lower right) regimes. However, the threshold for nitrate- and the ammonium-sensitive regime is not distinct in the small chemical range. Actually, the nitrate concentrations are sensitive to both precursors. The daily integrated nitrate production rate and averaged total ammonium concentrations for each city are denoted by the circles (Fig. 11b). The circles are located above the ridgeline, which means nitrate concentrations are more sensitive to the change of nitric acid production rate. Therefore, this scenario study highlights that the further mitigation of summertime particulate nitrate pollution should aim at the reduction of photochemical nitric acid production. For example, the reduction in NO_x emission could help to reduce the particulate nitrate pollution but may lead to enhancement in ozone pollution (see section 4.3). ”

Anonymous Referee #3

Received and published: 21 December 2018

This paper presents results from a 0-D box model constrained by observations of radical sources and sinks in order to evaluate the oxidation capacity of several Chinese megacities, including Beijing, Shanghai, Guangzhou, and Chongqing. The models suggest that while there are similarities in the chemistry of each urban area, such as ozone production being VOC-limited in each, there are some distinct differences in predicted radical concentrations, rates of ozone production, and OH reactivity, which may help provide insights into specific control strategies for each area.

While the paper provides some interesting contrasts between the cities, it is unfortunately somewhat difficult to read due to issues related to both the amount of information and how it is presented as well as style and grammar. In particular, section 3.3.2 describing the radical budget analysis reads more like a stream of thought rather than an organized discussion.

Answer:

The manuscript is restructured by moving the VOC description to section 4.1 and moving the OH-HO_2-RO_2 budget analysis (originally section 3.3.2) to section 4.2.

We have edited the manuscript substantially on the style and grammar and please find the modification in the revised manuscript.

A major assumption in the paper is that the model can accurately reproduce concentrations of OH, HO2, and RO2 radicals in order to predict the oxidation capacity of each region. Unfortunately, there is no discussion of whether this is a reasonable assumption. As mentioned in the introduction, previous measurements of radical concentrations in urban areas often exhibit significant discrepancies with model predictions, suggesting that chemical models are unable to accurately reproduce the oxidation capacity of these areas (see for example Whalley et al. (2018), Griffith et al. (2016), in addition to references cited in the Introduction). As summarized in the Lu et al. (2018) review cited in the paper, ": : :current tropospheric chemical mechanisms cannot explain the OH radical concentrations in China, which strongly underestimated the OH concentrations and the local ozone production for the low and high NOx range, respectively." The authors should expand the discussion of these discrepancies and discuss in much more detail their potential impact on their model predictions and conclusions.

Answer:

As shown in Rohrer, the OH is relative well captured by the model in moderate and high NOx regime. As the presented observation were conducted in megacities, which were mainly located in the high NOx regime. The model should be able to predict the OH concentrations well. The major question is the model underestimation for HO2 and RO2 concentrations and thus the local ozone production rate. We added sentences in Line 6 Page 7 “As previous field campaign in China shown that the OH concentrations could be underestimated in the low NO_x conditions (Tan et al., 2018b;Tan et al., 2017;Fuchs et al., 2017;Rohrer et al., 2014;Lu et al., 2013;Lu et al., 2012;Hofzumahaus et al., 2009). In this study, the NO_x concentration are in moderate and high range, where the model is capable to reproduce the OH concentrations relatively good (Rohrer et al., 2014). For the high NO_x regime, the prominent feature is the underestimation of HO_2 and RO_2 concentrations (Tan et al., 2018a;Tan et al., 2017;Tan et al., 2018d). This is also found in other urban site outside China (Griffith et al., 2016;Whalley et al., 2018;Kanaya et al., 2007;Dusanter et al., 2009;Shirley et al., 2006;Brune et al., 2016;Ren et al., 2013), indicating a common defect in current chemical mechanisms. Such model defect will lead to underestimation of local ozone production. The explanation of model underestimation is out of the scope of this study but the possible impact will be discussed in section 4.3.”

We also added the discussion on potential underestimation of $P(O_3)$ in Line 22 Page 12 “As mentioned in section 3.3, the current model could have defects for high NO_x conditions, which underestimated the peroxy radical concentrations and thus local ozone production China (Tan et al., 2017;Griffith et al., 2016;Whalley et al., 2018;Kanaya et al., 2007;Dusanter et al., 2009;Shirley et al., 2006;Brune et al., 2016;Ren et al., 2013). However, the quantitative estimation is not possible due to the absence of in-situ radical measurements. To our knowledge, no field campaigns have been conducted to perform in-situ radical measurements in city center area in China. However, a field campaign in downwind area of Beijing (YUFA) found local ozone production rate was underestimated due to the underestimation of HO_2 concentrations (Lu et al., 2010). Another field campaign in a rural site in NCP also found model underestimation of $P(O_3)$ by 20 ppbv per day compared a daily integrated ozone production of 110 ppbv derived from the measured HO_2 and RO_2 (Tan et al., 2017). Therefore, the ozone production rate presented derived from model calculations in this study should be considered as a lower limit. Nevertheless, the underestimation of peroxy radical concentration will not affect the O_3-NO_x-VOC sensitivity diagnosis (Tan et al., 2018d).”

Additional comments:

1) The paper would benefit from a more detailed description of what was measured and how they were measured, perhaps with a table in the supplement. In particular, the specific VOCs that were measured should be described in more detail.

Answer:

We added a table to describe the instrumentation in the supplement (Table S1). We also prepared the table in supplement to state what are measured, modelled, and parameterized in this study (Table S2). The measured VOCs and their concentrations are presented in table S3.

2) Instead of just showing the total AHC (or preferably AVOC as indicated elsewhere in the manuscript), it would be more informative to illustrate the diurnal mixing ratios of some important individual VOCs that demonstrate the similarities and differences in the areas as described in the manuscript.

Answer:

We changed all AHC to be AVOC in the revised manuscript.

We added a table about measured VOC in supplement (Table S3) and a table showing top 10 k_{OH} contributing VOCs (Table 2). The mean diurnal profiles of top 10 VOCs are added in supplement (Fig. S6). A detail discussion on the measured VOCs is added. Please find the answers in the response to referee #1 who has the similar comments.

3) In addition, it should be clarified which VOCs and/or OVOCs were measured and which were modeled as part of the radical budget. For example, were HCHO and other carbonyls measured or was their contribution to radical production based on modeled concentrations?

Answer:

The VOC are measured and OVOCs are modelled. Therefore, the alkene ozonolysis is observation constrained. We make this point clear by adding a sentence in the radical budget analysis section “”

We added the discussion of modelled OVOCs results in the end of section 4.1 VOC compositions and ozone production efficiency in the revised manuscript. The modelled OVOCs concentrations are comparable to previous studies for these regions, indicating the model is capable to reproduce the OVOCs formation. The added content is “The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations were in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012;Song et al., 2018;Chen et al., 2016;Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation.”

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~~Atmospheric~~Daytime atmospheric oxidation capacity in four Chinese megacities during photochemical polluted season: ~~radical budget and secondary pollutants formation~~a case study based on box model simulation

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Abstract. Atmospheric oxidation capacity is the core of converting freshly-emitted substances to secondary ~~pollutants.~~products, which are dominated by reaction with hydroxyl radicals (OH) during daytime. In this study, we present in-situ measurements of RO_x radical (hydroxy OH, hydroperoxy HO_2, and organic peroxy RO_2) precursors as well as products at four Chinese megacities (Beijing, Shanghai, Guangzhou, and Chongqing) during photochemical polluted seasons. The atmospheric oxidation capacity is evaluated using an observational-based model with the input of radical chemistry precursor measurements. The radical budget analysis illustrates the importance of HONO and HCHO photolysis, which contribute nearly half of the total primary radical sources. The radical propagation is efficient due to abundant NO in the urban environments. Hence, the production rate of secondary pollutants, i.e. ozone and fine particle precursors (H_2SO_4, HNO_3, and extreme low volatile organic compounds (ELVOCs)) is fast, resulting in secondary air pollution. The ozone budget demonstrates that strong ozone production occurs in the urban areas, which results in fast ozone concentration increases locally and through transport in downwind areas. The O_3-NO_x-VOC sensitivity tests show that ozone production is VOC-limited and that alkenes and aromatics should be first mitigated for ozone pollution control in the four megacities investigated. In contrast, NO_x emission control will lead to more severe ozone pollution due to the decrease of NO_x. For fine particle pollution, the role of HNO_3-NO_3- partitioning system is investigated with a thermal dynamic model (ISORROPIA2) due to the importance of particulate nitrate during photochemical polluted seasons. The strong nitric acid production converts efficiently to nitrate particles due to high RH and ammonia-rich conditions during photochemical polluted seasons. This study highlights the efficient radical chemistry that maintains the atmospheric oxidation capacity in Chinese megacities, which results in secondary pollution characterized by ozone and fine particles.

1. Introduction

Air pollution is the one of the major ~~threat~~threats to human health in cities (Kan et al., 2012). In China, the rapid economic development accompanied by degradation of air quality for the last decades in the eastern areas (Chan and Yao, 2008). More than 300 million people live in the North China Plain (NCP), Yangtze River Delta (YRD) and Pearl River Delta (PRD) regions in eastern China. Among all, Beijing, Shanghai, and Guangzhou are the metropolitan cities in these regions and suffering from severe air pollution. The Chengdu-Chongqing city group (population 90 million) locates in Sichuan Basin (SCB), southwest of China, representing the developing city clusters. Chongqing is the biggest city in the southwest of China, which suffers from severe air pollution as well. To improve the air quality, emission mitigations have been conducted since the 2000s. As a result, the primary pollutant concentrations ~~decline~~have declined since then. However, secondary pollution characterized by high concentrations of ozone and fine particle has become the major contributor to air pollution. The major composition of fine particles are secondary components (Tie et al., 2013;Sun et al., 2006;Huang et al., 2014;Guo et al., 2014;Cheng et al., 2016;Zheng et al., 2005;He et al., 2001;Sun et al., 2004), e.g. sulfate, nitrate, and oxidized organic aerosol. This indicates high oxidation capacity in the Chinese pollution environments. The national-wide measurements showed ozone is the only one out of six air quality index substance that increases in the last five years~~.~~ (Li et al., 2018c;Lu et al., 2018b). Therefore, it's difficult to control secondary pollution given the non-linear relation between primary and secondary pollutants. ~~After all,~~In contrast, the ozone pollution has been mitigated in the last decades due to efficient precursors emission control in U.S. (Parrish et al., 2017). The efficient ozone pollution control requires the knowledge of the role of oxidation processes on the secondary pollution formation because atmospheric oxidation capacity is the key factor that converts primary pollutants to secondary ones. ~~Therefore, it requires the knowledge of the role oxidation processes on the secondary pollution formation.~~

So far, only limited studies have been performed in China to elucidate the oxidation processes (Lu et al., 2018a)~~.~~(Lu et al., 2018a). The studies in 2006 found an OH source is missing in the current chemical mechanism for low NO_x conditions (Lu et al., 2012;Hofzumahaus et al., 2009;Lu et al., 2013). The study in Wangdu (summer) and Beijing (winter) found an evidence of missing RO_2 sources, which could lead to strong underestimation of ozone production (Tan et al., 2017;Tan et al., 2018c). The radical observation and model comparisons highlight the uncertainty of the radical chemistry in China. The nitrous acid (HONO) were measured and constraint to the model in these studies, which were the major source of the OH-HO_2-RO_2 radical system. However, the majority of HONO sources is unclear so far (Su et al., 2011;Ye et al., 2016;Li et al., 2014b). On the other hand, the large aerosol content offers a large surface to conduct heterogeneous reactions. Radical loss on the aerosol surface could also play a role, which is not well understood due to the limited information based on the Chinese aerosol composition. The Chlorine chemistry is gaining increasing attention recently, which acts as a radical source and source of particulate nitrate formation (Tham et al., 2016;Wang et al., 2016;Wang et al., 2017b;Wang et al., 2017c;Wang et al., 2017a). However, the large variability of uptake coefficient and $ClNO_2$ yield adds large uncertainty to heterogeneous reactions (Xue et al., 2014;Tham et al., 2018).

~~With respect to secondary formation, the radical chemistry is insightful to reveal the key processes. The ozone production rate can be determined by the oxidation rate of NO by HO_2 and RO_2 directly. The gas phase oxidation produced semi- and/or low volatile compounds, which are important precursors for particle formation. Sulfate, nitrate, and SOA are dominant contributors to the particle during heavy polluted episodes (haze events), all of which could be produced in the OH-initiated oxidation processes.~~

~~The Chengdu-Chongqing city group (population 90 million) locates in Sichuan Basin (SCB), southwest of China, representing the developing city clusters.~~ Although the new city clusters also suffer from air pollution, only sparse researches have been conducted in these regions, especially for the secondary pollution formation. For the SCB region, only limited studies have been performed regarding the oxidation capacity. Chengdu is evaluated using an observational-based model which found similar radical concentration and ozone production rate (Tan et al., 2018b). The VOC and ozone formation is evaluated in Chongqing (Su et al., 2018;Li et al., 2018b).

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In this study, we present the measurement at four megacities, Beijing, Shanghai, Guangzhou, and Chongqing. The focus of this study is to illustrate the atmospheric oxidation processes in the urban areas. AOC can be defined as the sum of respective oxidation rates of trace gases (VOCs, CO, and NOx) by the oxidants (OH, O_3, and NO_3) (Geyer et al., 2001). Given the relatively importance of OH oxidation during daytime, the AOC is restricted to OH oxidation in this study. The observation periods were selected in typical photochemical polluted seasons to explore the photochemistry and secondary pollution formation. An observational-based model is used to explore the oxidation capacity from the aspect of radical chemistry. This study aims to provide insight into the secondary pollution formation in Chinese megacities. With the intention to illustrate the common feature of the megacities oxidation capacity, we compared the results from different studies. Two questions need to be addressed in this study. First, what is the oxidation capacity in these megacities and which source(s) sustain it? Especially the comparison of city centers to suburban and rural locations, to foreign countries. Second, what is the secondary formation rate, e.g. ozone and nitrate? What is the limiting factor in secondary pollution formation? Finally, the diagnosis of atmospheric oxidation capacity and secondary pollution formation could provide fundamental knowledge for further air pollution control in China.

2. Methods

2.1 Measurement sites

This study presents the measurements at four Chinese megacities, namely Beijing, Shanghai, Guangzhou, and Chongqing. These cities ~~were~~are located in the highly polluted region (Fig. 1). Beijing, Shanghai, and Guangzhou are the main cities in North China Plain (NCP), Yangtze River Delta (YRD), and Pearl River Delta (PRD), which are representative of the most developed region in China. Chongqing is one of the biggest cities in southwestern China (population of 30 million), representing the Chinese developing city clusters.

The detail of the field campaigns is summarized in Table 1. All measurements sites locate within the city downtown areas to represent the conditions in the city center. Beijing is located on the north edge of the North China Plain and is the most north station (39.9 °N) than others. The campaigns were mainly conducted in summer to represent the most active photochemical season. The Beijing campaign took place in mid-summer (~~June~~July) and thus the strongest solar radiation input. The latitude of Shanghai (31.1 °N) and Chongqing (29.6 °N) are similar as well as the observation period (August). Therefore, the solar input level should be comparable. Given the synoptic flow pattern interaction, the atmospheric pollution is expected to be most serious in PRD in autumn (Zhang et al., 2007;Li et al., 2014a). The measurement in Guangzhou was performed in late October to represent the photochemical polluted period. However, the latitude is lowest (23.1 °N), which can partly compensate the seasonal effect. The maximum of 1-h averaged O_3 concentrations were more than 100 ppbv in Shanghai, Beijing, Guangzhou, but only 79 ppbv in Chongqing, which demonstrated a separation between the two classes of cities.

2.2 ~~instrumentation~~Instrumentation

In all sites, similar instrumentations were deployed as a standard super site. All Thermo instruments were carefully maintained and calibrated during the campaigns. Only a brief description of the measurement techniques is presented. Ozone was measured by UV absorption method using the Thermo O_3 analyzer (Model 49i). The NO_2 measurement was performed by the chemiluminescence ~~after~~ in the form of NO by chemical conversion using Molybdenum convertor. This conversion method is known to ~~NO.~~be interference by NO_z species, which could be converted to NO. Therefore, one should keep in mind that the NO_2 measurement presented in this study could be positive biased from the ambient NO_2 concentrations. CO was measured by the infrared absorption technique using Thermo instrument (Model 20). The performance of different instruments is summarized in Table S1. Speciated VOCs measurement was performed by the GC-MS/FID. VOC measurements (including 55 organic species) were performed by commercial an instrumentation using gas chromatograph (GC) equipped with a mass spectrometer (MS) and a flame ionization detector (FID). In principle, the air sample was drawn into two parallel channels for enrichment by cooling before analysis (Wang et al., 2014). The VOCs measurements include C_2–C_{11} alkanes, C_2–C_6 alkenes, and C_6–C_{10} Aromatics (Table S2). The photolysis frequencies were measured by spectrum radiometer. Meteorological parameters were measured simultaneously, e.g. ambient temperature, pressure, and relative humidity.

2.3 The model

A box model based on the Regional Atmospheric Chemical Mechanism version 2 (Goliff et al., 2013) is used to simulate the concentrations of the ~~short-lived~~ OH, HO_2 and RO_2 radicals concentrations and other unmeasured secondary species concentrations. The newly proposed isoprene mechanisms are also incorporated (Peeters et al., 2014;Fuchs et al., 2013). The model was constrained to the observation of photolysis frequencies, long-lived trace gases (NO, NO_2, O_3, CO, C_2−C_{12} VOCs), and meteorological parameters. Since nitrous acid (HONO) was not measured in these campaigns, it was fixed to 2% of the observed NO_2 concentrations because good correlation was found between HONO and NO_2 in different field studies with a constant ratio being 0.02 ~~(Elshorbany et al., 2012).~~(Elshorbany et al., 2012). The uncertainty of such parameterization is discussed in section ~~3.3.2~~4.2. The measured, modelled and parameterized parameters are summarized in Table S3. The uncertainty of the model calculations depends on the model constraints and the reaction rate constants. Taking into account the uncertainties of both measurements and kinetic rate constants, the model calculations is approximately 40% (Tan et al., 2017).

3. Results

3.1 Overview of measurements

The mean diurnal profiles of measured ambient temperature, j(O^1D), and CO, O_3 (O_x = O_3+NO_2), NO_x(=NO+NO_2), and ~~AHC~~AVOC concentrations are shown in Fig. 2 (the time series are shown in Fig. S1-S4). The ambient temperature is relatively similar in Beijing, Shanghai, and Chongqing, but lower in Guangzhou because the campaign was conducted in a later time of a year. Similarly, the photolysis frequencies are smaller in Guangzhou. However, j(O^1D) is highest in Beijing and are comparable in Shanghai and Chongqing. However, diurnal maximum O_3 concentrations are highest in Shanghai (80 ppbv) followed by Beijing (72 ppbv), Guangzhou (65 ppbv), and Chongqing (56 ppbv). The diurnal peak of O_3 appears at 15:00~16:00 LT in Beijing, Guangzhou, and Chongqing. In Shanghai, the peak of O_3 shows up at 13:00 LT due to the fast increase in the morning. During the measurement period, the observed ozone concentrations exceed the Chinese National Air Quality Standard Grade II (99.3 ppbv) in Beijing, Shanghai, and Guangzhou (Table 1).

When a measurement site is close to NO_x emission sources, part of the O_3 is titrated to NO_2 by fresh emitted NO. Although O_3 is regenerated in a few minutes to half hour after the photolysis of NO_2, O_3 is stored temporally in the form of NO_2. Therefore, O_x, the sum of O_3 and NO_2, is a better metric to describe ozone pollution in the urban area. O_x concentrations are also shown with broken lines in Fig. 2. In this case, the O_x mean diurnal profiles in Beijing, Shanghai and Guangzhou show maximum values of about 90 ppbv (1-hour resolution), indicating the ozone pollution are comparable in these cities during the measurement period. In Chongqing, the maximum of the diurnal average is 66 ppbv. The ozone pollution is serious in autumn in Guangzhou due to the unique synoptic system, including the surface high-pressure system, hurricane movement and the sea-land breeze (Fan et al., 2008). In Shanghai, the synoptic weather is crucial to pollution accumulation, and the ozone concentrations are reduced in August and September due to the cleaning effect by the summer Monsoon (Dufour et al., 2010;Geng et al., 2015).

Given the relatively short periods for these campaigns, one concern is about the representativeness of measurements. We compared the observation from these intensive campaigns to the routine measurement obtained in the environmental monitor stations operated by the Chinese environmental protection agency (Fig. S5). We found that the mean diurnal profiles of O_3 and O_x obtained in all sites are comparable to the highest monthly averaged diurnal profiles for the same city (bias < 20%). The relatively small O_3 and O_x concentrations observed in Chongqing compared to other cities (Fig. 2) is consistent with the environmental monitor stations observation (Fig. S5). Therefore, it suggests that the ozone pollution is less severe in Chongqing compared to the megacities in eastern China.

The ozone precursors, NO_x, and AVOCs are shown in Fig. 2. In all cases, the NO_x concentrations show a typical diurnal profile with a minimum in the afternoon. In the morning, the peak is caused by the transportation emission during the rush hours. In Shanghai, the nighttime NO_x concentrations also decrease after sunset but increase after midnight, which anti-correlates with the O_3. The AVOCs concentrations show similar diurnal profiles as those of NO_x, which suggests both AVOCs and NOx are originated from the same sources, e.g. traffic emission and/or manipulated by the same factor, e.g. boundary layer development. CO is also a precursor of ozone. The diurnal profiles of CO are almost flat due to their long lifetime versus OH. A small peak appears in the morning rush hours due to poor dilution condition and enhanced emission from transportation.

3.2 OH reactivity and composition

OH reactivity (k_{OH}) represents the pseudo first-order reaction rate constant of OH radical. It is a measure of the sum of sink terms due to OH radical reactants X_i, which depends on their ambient concentration $[X_i]$ and their rate coefficient with OH radical. Mathematically, k_{OH} equals to the inverse of ambient OH radical lifetime. The use of OH reactivity is of importance to understand the OH consumption potential.

The mean diurnal profiles of OH reactivity calculated from a box model are presented in Fig. 3, including the contribution from CO, NO_x, VOCs, and model generated secondary species. In general, the OH reactivity is lowest in the afternoon and highest in the morning rush hours due to the change of dilution condition over a day.

In this study, the modeled OH reactivity in Guangzhou is highest (20-30 s^{-1}) among all the cities (Fig. 3), indicating a strong influence of anthropogenic emission in Guangzhou. In Beijing and Chongqing, OH reactivity is comparable, in the range of 15 to 25 s^{-1}. ~~The total OH reactivity can be measured directly with three techniques (Fuchs et al., 2017). In China, OH reactivity measurements were performed~~In Shanghai, the OH reactivity was lowest (<15 s^{-1}) due to the small contribution from CO and NO_x. Previous field campaigns performed OH reactivity measurements in NCP and PRD, showing large seasonal and spatial variation. In Beijing, k_{OH} measurements were conducted in an urban and suburban site during summer (Lu et al., 2013;Williams et al., 2016;Yang et al., 2017). The OH reactivity was on average in the range of 10 to 30 s^{-1} and showed large daily variation due to the meteorology changes. In PRD, OH reactivity was measured in a rural site (Backgarden) in summer and suburban site (Heshan) in autumn, both of which were close to megacity Guangzhou (<100km). In Backgarden, the average OH reactivity was in the range of 20 to 50 s^{-1} with a large contribution from isoprene (Lou et al., 2010). In Heshan, downwind of Guangzhou, OH reactivity was dominated by anthropogenic species. However, the averaged k_{OH} was comparable in two sites (Tan et al., 2018a).

~~In this study, the modeled OH reactivity in Guangzhou is highest (20-30 s^{-1}) among all the cities (Fig. 3), indicating a strong influence of anthropogenic emission in Guangzhou. In Beijing and Chongqing, OH reactivity is comparable, in the range of 15 to 25 s^{-1}.~~ In Chengdu, another big city in southwestern China, the modeled OH reactivity was also found to be in the range of 15 to 30 s^{-1} at three urban sites, with an exception that large OH reactivity was contributed by alkenes due to petrochemical complex industry (Tan et al., 2018b). ~~In Shanghai, the OH reactivity was lowest (<15 s^{-1}) due to the small contribution from CO and NO_x.~~

The ~~speciation is~~contributions of different OH reactivity are clearly shown in Fig. 4. The contribution of OH reactivity was relatively similar among all cities as a typical fingerprint of anthropogenic emission. NO_x is the most important OH reactants that contribute 28%~35% to the total reactivity. In total, the inorganic species (CO and NO_x) contribute more than half of the reactivity. The measured AVOCs contribute to the total OH reactivity from 14% to 26%. In Beijing, the AVOC contribution is lowest as well as the absolute reactivity (2.3 s^{-1}). In Guangzhou, the contribution and absolute reactivity of AVOC (6 s^{-1} compared to 2~3 s^{-1} in other cities) are highest. However, isoprene is relatively small in Guangzhou (0.4 s^{-1}) due to the observation season. In comparison, isoprene reactivity is up to 1 s^{-1} in Beijing and Chongqing but becomes negligible in Shanghai. The small isoprene concentration was also reported in another study (Geng et al., 2011).

3.3 Modelled OH-HO_2-RO_2 Radical concentrations

The OH, HO_2, and RO_2 concentrations are derived from box model calculations (Fig. S1-S4). The mean diurnal profiles are shown in Fig. 5. Modeled OH concentrations show distinct diurnal variation in all campaigns. The peak of OH mean diurnal profile is highest in Beijing and Shanghai (7×10^6 cm^{-3}). The peak is 4×10^6 cm^{-3} in Chongqing and further decrease to 2×10^6 cm^{-3} in Guangzhou. The relative change of OH maximum is consistent with the observed photolysis frequencies (Fig. 2). In fact, modeled OH concentrations show good correlation with the observed $j(O^1D)$ (R=0.83, 0.93, 0.87, and 0.87 for Beijing, Shanghai, Guangzhou, and Chongqing) because OH chemistry relies on solar radiation input tightly. The OH maximum ranking is consistent with that of $j(O^1D)$. The $j(O^1D)$-OH correlation slope was largest in Shanghai (3.0×10^{11} $cm^{-3}s^{-1}$ compared to 2.0×10^{11} $cm^{-3}s^{-1}$ in the other cities) because the OH reactivity is lower and OH lifetime becomes longer. The good correlation between OH and $j(O^1D)$ was found in other field campaigns conducted in China with a correlation coefficient more than 0.8 (Tan et al., 2017;Rohrer et al., 2014;Lu et al., 2013;Lu et al., 2012). However, the correlation slopes were about $(4.5\pm0.5)\times10^{11}$ $cm^{-3}s^{-1}$, which are on average two times larger than the modeled results in this study. The different slopes could be due to the different chemical regimes in each location. The larger factor was found in suburban and rural sites, where the air masses were more oxidized. The slope is comparable to the results obtained in urban environments where the slope was in the range of $(2\text{-}4)\times10^{11}$ $cm^{-3}s^{-1}$ (Holland et al., 2003;Michoud et al., 2012;Griffith et al., 2016;Whalley et al., 2018).

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The peroxy radical concentrations are variable in different campaigns depending on the chemical conditions. A general feature is found in all cases that peroxy radical concentrations are suppressed in the morning. Since then, peroxy radical concentration increases gradually and reach a peak at about 14:00 (two hours later than the maximum of solar radiation), because of the suppression by high NO. The peroxy radicals concentrations are highest in Chongqing with a maximum of mean diurnal profiles being 5×10^8 cm^{-3} for HO_2 and 7×10^8 cm^{-3} for RO_2. Meanwhile, the HO_2 and RO_2 concentrations are comparable in the other cities despite the difference in the solar radiation and chemical conditions. In Chongqing, the relative large VOC/NO_x ratio leads to the highest peroxy radical concentration in the model, which reflects in the efficient radical recycling and ozone production.

As previous field campaign in China shown that the OH concentrations could be underestimated in the low NO_x conditions (Tan et al., 2018a;Tan et al., 2017;Fuchs et al., 2017;Rohrer et al., 2014;Lu et al., 2013;Lu et al., 2012;Hofzumahaus et al., 2009). In this study, the NO_x concentration are in moderate and high range, where the model is capable to reproduce the OH concentrations relatively good (Rohrer et al., 2014). For the high NO_x regime, the prominent feature is the underestimation of HO_2 and RO_2 concentrations (Tan et al., 2017;Tan et al., 2018d). This is also found in other urban site outside China (Griffith et al., 2016;Whalley et al., 2018;Kanaya et al., 2007;Dusanter et al., 2009;Shirley et al., 2006;Brune et al., 2016;Ren et al., 2013), indicating a common defect in current chemical mechanisms. Such model defect will lead to underestimation of local ozone production. The explanation of model underestimation is out of the scope of this study but the possible impact will be discussed in section 4.3.

4. Discussion

4.1 VOC compositions and ozone production efficiency

The relative contributions of grouped VOCs are shown in Fig. ~~5~~6. Anthropogenic VOCs are usually more important than the biogenic ones. The isoprene accounted for 15% of the measured VOC reactivity in Beijing and Chongqing. The shares of different VOCs groups are comparable with a slightly different portion of alkanes and alkenes. Aromatics become the most important VOC group in Guangzhou, accounted for about half of the measured VOC reactivity, which is related to vehicle emissions and industry that produce VOC-related products (Zheng et al., 2009).

The OH reactivity concept is useful to estimate the ozone production for VOCs because it describes the VOC degradation rate initiated by OH oxidation that leads to net ozone production in the presence of NO and sunlight (see section 4.1). On the other hand, the ozone formation potentials (OFPs) are used to describe the theoretical ozone production maximum. This metric shows the temporal Lagrangian evolution of O_3 production potential within a mixture of air that undergoes fully oxidation. The OFP of individual VOCs is calculated by the product of measured VOC concentrations and its MIR value (Carter, 2009), which are sum up later according to the VOC classification. Aromatics become dominant species in the OFPs due to their large carbon numbers and thus high MIR values. In Guangzhou, aromatics contributed up to 70% of the share of OFPs, followed by Shanghai (55%), Beijing (43%), and Chongqing (42%).

In comparison, the mixing ratios of different VOC are shown. It is worth noting that alkanes (including ethyne) accounted for a large fraction in the mixing ratio, their contribution to OFPs and OH reactivity was small. Therefore, they are not important in ozone formation and radical chemistry. It highlights the importance of the concept of OH reactivity and OFPs to describe photochemical processes accurately.

~~3.3 OH-HO_2-RO_2 Radical concentrations and budget analysis~~

~~3.3.1 Concentrations~~

~~The OH, HO_2, and RO_2 concentrations are derived from box model calculations (Fig. S1-S4). The mean diurnal profiles are shown in Fig. 6. Modeled OH concentrations show distinct diurnal variation in cases. The maximum of OH means the diurnal profile is largest in Beijing and Shanghai (7×10^6 cm^{-3}). The maximum is 4×10^6 cm^{-3} in Chongqing and further decrease to 2×10^6 cm^{-3} in Guangzhou. The relative change of OH maximum is consistent with the observed photolysis frequencies (Fig. 2). In fact, modeled OH concentrations show good correlation with the observed j(O^1D) (R=0.83, 0.93, 0.87, and 0.87 for Beijing, Shanghai, Guangzhou, and Chongqing) because OH chemistry relies on solar radiation input tightly. The OH maximum ranking is consistent with that of j(O^1D). The j(O^1D)-OH correlation slope was largest in Shanghai (3.0×10^{11} $cm^{-3}s^{-1}$ compared to 2.0×10^{11} $cm^{-3}s^{-1}$ in the other cities) because the OH reactivity is lower and OH lifetime becomes longer. The good correlation between OH and j(O^1D)~~

~~was found in other field campaigns conducted in China with a correlation coefficient more than 0.8 (Tan et al., 2017;Rohrer et al., 2014;Lu et al., 2013;Lu et al., 2012). However, the correlation slopes were about (4.5±0.5)×10^{11} $cm^{-3}s^{-1}$, which are on average two times larger than the modeled results in this study. The larger correlation slope suggests that solar radiation converts more efficiently to radical concentrations. The different conversion factor could be due to the different chemical regimes in each location. The larger factor was found in suburban and rural sites, where the air masses were more oxidized. The slope is comparable to the results obtained in urban environments where the slope was in the range of (2-4)×10^{11} $cm^{-3}s^{-1}$ (Holland et al., 2003;Michoud et al., 2012;Griffith et al., 2016;Whalley et al., 2018).~~

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~~The peroxy radical concentrations are variable in different campaigns depending on the chemical conditions. A general feature is found in all cases that peroxy radical concentrations are suppressed in the morning. Since then, peroxy radical concentration increases gradually and reach a peak at about 14:00 (two hours later than the maximum of solar radiation), because of the suppression by high NO. The peroxy radicals concentrations are highest in Chongqing with a maximum of mean diurnal profiles being 5×10^8 cm^{-3} for HO_2 and 7×10^8 cm^{-3} for RO_2. Meanwhile, the HO_2 and RO_2 concentrations are comparable in the other cities despite the difference in the solar radiation and chemical conditions. In Chongqing, the relative large VOC/NO_x ratio leads to the highest peroxy radical concentration in the model, which reflects in the efficient radical recycling and ozone production.~~

~~3.3~~The top 10 OH reactivity contributing VOCs are summarized in Table 2. The order of importance is sorted by the averaged OH reactivity for four cities. Among all, propene are the most important OH reactivity contributor, which contributed about 0.4~0.6 s^{-1} (Table 2). The small VOCs (propene, ethane, ethene) are relatively important with respect to OH reactivity. 9 out of the top 10 VOCs are alkenes and aromatics (except ethane). In Guangzhou, the xylene (m,p-, and o-) and toluene are also important OH reactants, consistent with the inventory study (Zheng et al., 2009). The diurnal profiles are shown in Fig. S6. The observed anthropogenic VOC concentrations show typical diurnal profile that increase during night and decrease during afternoon. One exception is Shanghai site, the mean diurnal profiles of propene and 1,2,4-trimethybenzene are flat, while that of styrene shows peak around noontime, indicating unique VOC emission feature in that site.

The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations are in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012;Song et al., 2018;Chen et al., 2016;Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation.

4.2 $OH-HO_2-RO_2$ Radical budget analysis

All radical reactions are classified into four groups (initiation, termination, propagation, and thermos-equilibrium with reservoir species). The reaction turnover rate illustrates the important processes in the RO_x radical reactions framework. The initiation and termination rate are shown in Fig. 7. The following radical budget analysis will focus on the daytime conditions (06:00—18:00) if no additional clarification.

The dominant radical sources are photolysis reactions, including HONO, O_3, HCHO and other carbonyl compounds. The photolysis of HONO and O_3 (producing O^1D and followed by H_2O reaction) produce OH radicals, which contributes 33-45% to the total primary source, $P(RO_x$~~).~~) among all campaigns. The HCHO photolysis produces HO_2 (14-33% of $P(RO_x)$) while the other carbonyl compounds ~~photolyze to~~generate RO_2 radicals (3-6% of $P(RO_x)$). Therefore, photolysis reactions dominate the radical primary sources during daytime (58-86%). In contrast, alkenes ozonolysis is the dominant radical source during nighttime and the yields of OH, HO_2, and RO_2 radicals depend on individual alkenes. The maximum of $P(RO_x)$ mean diurnal profile is largest in Beijing (5 ppbv/h), followed by Shanghai (4.6 ppbv/h) and Chongqing (4.3 ppbv/h). The daytime averaged P(RO_x) is smaller in Shanghai due to the narrower peak of photolysis frequencies (Fig. 2) and shorter photolysis reaction time. The primary radical source is smallest in Guangzhou (3.2 ppbv/h) due to the later observation period in a year. However, the alkene ozonolysis contributed significantly to the radical sources in Guangzhou (43% of the total primary source for daytime conditions), which could attribute to higher abundance of alkenes due to special emission inventory (see section 3.2).

The ozonolysis reactions mainly contributed by trans-2-butene in Beijing (55%), Guangzhou (42%), and Chongqing (39%), whose concentrations are in the range between 0.1 to 0.3 ppbv (Fig. S6). Although trans-2-butene is only the 8th important VOCs with respect to OH reaction (Table 2), it become the most important O_3 reactants producing RO_x radicals due to its fast reaction rate with O_3 (1.9×10^{-16} $cm^{-3}s^{-1}$ compared to 1.0×10^{-17} $cm^{-3}s^{-1}$ of propene, rate constant derived from MCM3.3.1 (http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt)). In Shanghai, propene becomes the most important alkene with respect to O_3 reaction, which accounts for about 42% of the total alkene ozonolysis reactions. Actually, the relatively high contribution from alkene ozonolysis to the RO_x radical primary sources could be one of the important characteristics for RO_x radical primary sources in Chinese megacity. The importance of alkene ozonolysis was also found in Santiago, Chile (Elshorbany et al., 2009) and Essex, UK (Emmerson et al., 2007), where alkene ozonolysis contributed about 20% to the total radical primary production.

Radical termination can be divided into two groups, the nitrogen-containing compounds, including HONO, HNO_3, $RONO_2$, and PAN-type species (L_N). The other pathway leads to peroxides formation result from the combination of two peroxy radicals (L_H). The ratio between L_N and L_H depends on the NO_x concentrations. In urban environments, the limiting factor for radical propagation is the abundance of VOCs. In our case, the radical termination is dominated by L_N (>70%). Among all, the nitric acid formation was the major contributor to the radical termination in all cities (>50%). In Chongqing, the peroxide formation path contributes 26% to the radical termination, especially the ratio increase to 32% during the afternoon due to the higher VOC/NO_x ratio. Net PAN-type species formation as a radical loss becomes relatively important in Guangzhou (about 20%) due to the lower temperature (Fig. 2). It is reported that on average 25% of the radical can be lost via forming PAN-type species in Beijing during winter (Tan et al., 2018c). Besides, PAN-type species formation becomes important in the urban area, e.g. it contributes 30% to the total radical loss in London downtown area (Whalley et al., 2018).

The comparison of the four cities is clearly shown in Fig. 8. The HONO photolysis is the dominant OH source in all cities except in Shanghai. The O_3 photolysis is more important than HONO photolysis in Shanghai, contributing 55% to the total OH primary sources and 23% of the total radical sources. In all cities, the primary production of HO_2 is comparable to that of OH, which is mainly contributed by the HCHO photolysis and alkene ozonolysis. These results are consistent with the model calculation performed in Beijing (Yang et al., 2018) and Hong Kong (Xue et al., 2016). The importance of HONO and HCHO photolysis to radical primary production is also found in suburban and rural environments (Lu et al., 2012;Lu et al., 2013;Tan et al., 2017). In the base model scenario, HONO is scaled to NO_2 measurements and the uncertainty of this assumption is further discussed following. In the base model, the HONO concentrations are scaled to the observed NO_x concentration using a scaling factor 0.02 ~~(Elshorbany et al., 2012)~~. In this study, we use this scaling factor between HONO and NO_x to simplify the discussion of unknown HONO sources. In the original RACM2 model, only homogenous source is included, i.e. $OH+NO\rightarrow HONO$, which is not sufficient to support the high daytime HONO concentrations and, as a result, leads to a strong underestimation of OH concentrations (Su et al., 2011;Yang et al., 2014;Tong et al., 2016;Ye et al., 2016;Li et al., 2012;Li et al., 2014b). Although the HONO to NO_2 ratio is relative robust and constant as reported in other field campaigns (Elshorbany et al., 2012), such simple parameterization could increase the uncertainty of our model calculation. To further investigate the uncertainty from this simple parameterization, the scaling factor is varied from 0.015 to 0.03. The modelled OH concentrations change by less than 10 % if the HONO scaling factors change by 50% (Fig. S8). Besides, the modelled HO_2 and RO_2 concentrations are relatively stable with different HONO scaling factors. The different scaling factors also have impact on the model generated species, e.g. HCHO (Table S4). In fact, the higher HONO concentrations lead to more active photochemical reactions and more HCHO production. The higher HCHO concentrations could further enhance the photochemistry by more radical photolytic sources in return. Therefore, the higher (lower) modelled radical concentrations due to increase (reduce) the HONO scaling factors are also affected by the corresponding change in modelled HCHO concentrations. This demonstrates the nonlinearity of the photochemical system. Nevertheless, the parameterized HONO concentrations are in the range of 0.3 to 0.6 ppbv during daytime (Table S4), which are consistent with previous in-situ measurements in urban areas (Lu et al., 2013;Li et al., 2010;Ren et al., 2003;Kanaya et al., 2007). To evaluate the impact of missing HONO source on the radical chemistry, we switched off the scaling between HONO and NO_x in a sensitivity test~~.~~ (Fig. S8). Therefore, the results show that OH concentrations reduce by about 20% if the only homogenous source is considered. The modeled HO_2 and RO_2 concentrations are also reduced ~~correspondingly (~~by 15-20~~%).~~ % (Table S4).

~~The RO_2 source strength is in the range of 0.2 to 0.3 ppbv/h, which is balanced by the RO_2 loss via organic nitrate formation ($RONO_2$). Therefore, the imbalance between primary source and termination of HO_2 (P>D) results in a net flow from HO_2 to OH. Since the sum of RO_x initiation and termination rate should be balanced, the excess HO_2 radical production leads to the large formation of nitric acid through the net flow from HO_2 to OH. The equilibrium between RCO_3 (acetyl peroxy radicals) and PAN-types species tends to result in a radical loss (0.1~0.3 ppbv/h). The equilibrium between HO_2 and HNO_4 is fast with null effect on the radical budget.~~

The RO_2 primary source strength is in the range of 0.2 to 0.3 ppbv/h, which is mainly contributed by alkene ozonolysis and OVOC photolysis (Fig. 8). In this study, the OVOC photolysis mainly includes carbonyl-containing compounds (e.g. acetaldehyde, aldehydes with carbon numbers larger than 3), which are generated by the box model. The modelled acetaldehyde concentrations are in the range of 2 to 4 ppbv (Fig. S7), consistent to the observations in Beijing (Chen et al., 2016) and Hong Kong (Lyu et al., 2016). The photolysis rate of carbonyl-containing compounds (except HCHO) is about one third to a quarter of the HCHO photolysis rate. In comparison, this ratio could be close to or even higher than 1 in other urban studies (Ren et al., 2013;Volkamer et al., 2010;Emmerson et al., 2007;Michoud et al., 2012;Whalley et al., 2018;Xue et al., 2016). In contrast, the relatively small contribution from other carbonyl-containing compounds photolysis than HCHO photolysis were reported in an urban and suburban site in Hong Kong (Lyu et al., 2016), where the acetaldehyde concentrations were about 1 to 2 ppbv, comparable to our model simulation. Such large discrepancy in the role of other OVOC photolysis to the radical production highlights the importance to measure these radical precursors in the future studies.

The OH reacts with VOCs or CO and produces peroxy radicals. The peroxy radicals react with NO producing NO_2, which lead the net production of O_3 in the presence of sunlight (see section 4.~~1~~3). Nitric acid can be formed from the reaction between NO_2 and OH, which is an important precursor of fine particles (see 4.~~2~~4). Therefore, the efficient radical propagation facilitates the secondary pollution formation.

In addition, the radical propagation between OH, HO_2, RO_2, RCO_3 are also shown in the inner part of Fig. 8. In RACM2, RCO_3 is mainly produced in the reaction between OH radical and aldehydes. RCO_3 is separated from the sum of RO_2 family and explicitly shown in the radical propagation because RCO_3 reacts with NO and converts to RO_2. In the sum of RO_2 concentrations, RCO_3 is considered as a subgroup of RO_2 radicals (e.g. Fig. ~~6~~5).

~~The OH reactions with CO and VOC produce to HO_2 and RO_2, respectively.~~ The conversion from OH to RO_2 is slightly faster than OH to HO_2. In addition, the conversion from OH to RCO_3 is about one-third of the rate from OH to RO_2. In the presence of NO, OH is regenerated from peroxy radicals and ozone is produced in the same process~~ (see section 3.5).~~. The flow rate from RO_2 to HO_2 is less than half of the flow rate from HO_2 to OH. Even considering the contribution from RCO_3+NO, RO_2 (+RCO_3) contributes less than half of the P(O_3). Surprisingly, the HO_2 contribution to the total ozone production is constant at 63% in all cases. In this study, we find that the ratio between $P(O_3)$ and k_{voc}×[OH] is rather constant in the range of 1.5 to 1.6. Therefore, the robust relation between OH oxidation and ozone production indicates that it would be justified to estimate the ozone production rate using the reaction rate of OH+VOC (CO) in the future. However, the nature of such a robust relation ~~need~~needs to be investigated before real application.

4.~~1~~3 Ozone production and sensitivity

4.~~1~~3.1 Local ozone production

Ozone is generated from the NO_2 photolysis, which produces NO simultaneously. The removal of NO without consuming O_3 leads to net ozone production. In the photochemical system, peroxy radicals (HO_2 and RO_2) are the major NO consumers in all photochemical reactions.

In this study, the ozone formation rate $F(O_3)$ is calculated from the NO oxidation rate by HO_2 and RO_2 radicals as denoted in E2.

$$F(O_3) = k_{HO_2+NO} \cdot HO_2 \cdot NO + k_{(RO_2+NO)eff} \cdot RO_2 \cdot NO \qquad \text{(E2)}$$

The chemical loss of O_3 includes O_3 photolysis (producing O^1D followed by H_2O reaction) and its reactions with alkenes, OH, HO_2 (E3). Since NO_2 can be regarded as a reservoir species of O_3, the reaction between NO_2 and OH is also considered as ozone chemical loss. In fact, the use of O_x is helpful to avoid the interruption of NO titration due to fresh emission, which is conservative to describe the ozone concentration change due to photochemical reactions (Liu, 1977).

$$D(O_3) = [O^1D][H_2O] + (k_{O_3+OH}[OH] + k_{O_3+HO_2}[HO_2] + k_{O_3+alkenes}[alkenes])[O_3] + k_{OH+NO_2}[OH][NO_2] \qquad \text{(E3)}$$

Therefore, the net ozone production rate $P(O_3)$ is determined by the difference between E2 and E3. The mean diurnal profiles of $P(O_3)$ are shown in Fig. 9. The ozone production rate is highest in Beijing and Shanghai with a diurnal averaged maximum reaching 19 ppbv/h. Although the peroxy radical concentrations are highest in Chongqing, the ozone production rate only shows a board peak at 13 ppbv/h. The duration of ozone production is different with the longest duration in Beijing (13 hours). Therefore, the daily integrated ozone production rate is largest in Beijing (136 ppbv). For comparison, the integrated ozone production rate were 92, 40, and 105 ppbv in Shanghai, Guangzhou, and Chongqing, respectively.

The O_x concentration change depends on both the local production and physical processes (E4). $R(O_3)$ represents the combined effect of all physical processes, including horizontal transportation, vertical mixing, deposition and so on.

$$\frac{d(O_x)}{d(t)} = P(O_3) + R(O_3) \qquad \text{(E4)}$$

As shown in Fig. 9, the O_x concentration changes are derived from the derivative of observed O_x concentrations. In Beijing, Guangzhou, and Chongqing, the $d(O_x)/dt$ show similar increasing trends in the morning starting at 06:00 (Fig. 9). In Shanghai, positive derivative shows up at 05:00, one hour earlier than the other three cities. Also, the increase rate is fastest in Shanghai during the morning hours. However, $d(O_x)/dt$ turn sharply from positive to negative at 12:00 in Shanghai. While positive $d(O_x)/dt$ last until 16:00 in the other three cities. The difference in the $d(O_x)/dt$ results in an early O_x peak (around noon time) in Shanghai. In the bottom panel of Fig. 9, the difference between $d(O_x)/dt$ and $P(O_3)$ are shown, which denotes the local transportation of O_x (positive: inflow; negative: outflow). In Beijing and Chongqing, the local production rate is larger than the O_x concentration increase. Hence, it suggests that the photochemical produced O_x at the measurement site is transported to downwind regions. In Shanghai and Guangzhou, both positive and negative values appear during daytime, indicating the local ozone budget changes from importation to exportation. In the morning, the increases in O_x concentrations are larger than the local ozone production rate, which is supported by additional O_x import from the volume outside. The O_x is most likely entrained from the air aloft because the raising up boundary layer mixes in the air mass aloft from the residual layer, which maintains the high load of O_x that produced from the last day and then isolated from the surface layer. Especially in Shanghai, the fast O_x concentration increase before 08:00

is mainly caused by transportation given the relatively small local production rate. The O_x import stops at about 10:00 and the surface layer becomes a net O_x source region. The O_x importation also stops in the later time of a day (at about 14:00) in Guangzhou. The O_x transportation to downwind areas (negative $R(O_3)$) are observed in Beijing, Shanghai, and Chongqing during the afternoon, and in Guangzhou after sunset, which suggest the city centers are important for O_x formation in a regional scale.

~~4.1.2 O_3-NO_x-VOC sensitivity~~

As mentioned in section 3.3, the current model could have defects for high NO_x conditions, which underestimated the peroxy radical concentrations and thus local ozone production China (Tan et al., 2017;Tan et al., 2018d;Griffith et al., 2016;Whalley et al., 2018;Kanaya et al., 2007;Dusanter et al., 2009;Shirley et al., 2006;Brune et al., 2016;Ren et al., 2013). However, the quantitative estimation is not possible due to the absence of in-situ radical measurements. To our knowledge, no field campaigns have been conducted to perform in-situ radical measurements in city center area in China. However, a field campaign in downwind area of Beijing (YUFA) found local ozone production rate was underestimated due to the underestimation of HO_2 concentrations (Lu et al., 2010). Another field campaign in a rural site in NCP also found model underestimation of $P(O_3)$ by 20 ppbv per day compared a daily integrated ozone production of 110 ppbv derived from the measured HO_2 and RO_2 (Tan et al., 2017). Therefore, the ozone production rate presented derived from model calculations in this study should be considered as a lower limit. Nevertheless, the underestimation of peroxy radical concentration will not affect the O_3-NO_x-VOC sensitivity diagnosis (Tan et al., 2018c).4.3.2 O_3-NO_x-VOC sensitivity

The OH-HO_2-RO_2 radical budget is useful to diagnose the O_3-NO_x-VOC sensitivity as discussed in section 3.3.2. In this section, we use the ratio of nitrate formation rate (L_N) to total radical production/termination rate (Q), known as L_N/Q ratio to evaluate the ozone production sensitivity as suggested by Kleinman et al. (1997). The threshold is 0.5 of the L_N/Q ratio. When L_N/Q is greater than 0.5, the radical termination is outweighed by the nitrate formation which indicates the ozone production is in limited to VOCs abundance; On the other hand, when L_N/Q is less than 0.5, peroxy radicals self-combination dominates radical termination indicating ozone production is under NO_x-limited control. In the radical budget analysis, we found the L_N contributed more than 70% to the radical termination in all cities. With a larger than 0.5 L_N/Q ratio, ozone production was in VOC-limited regime, which persist in all the cities in this study.

The Relative Incremental Reactivity (RIR) method is also used to evaluate the O_3-NO_x-VOC sensitivity. RIR is a useful metric for ozone sensitivity to individual precursors. The model input parameters are changed by a certain amount and the corresponding ozone concentration change is compared and summarized to reveal the O_3-NO_x-VOC sensitivity. The calculation of RIR is expressed in E5.

$$\mathrm{RIR(X)} = \frac{\Delta \mathrm{O_3(X)/O_3}}{\Delta \mathrm{C(X)/C(X)}} \qquad \text{（E5）}$$

In equation 1, X represents a set of primary pollutants and O_3 represents the modeled O_3 concentrations in the base case. $\Delta C(X)/C(X)$ represents the relative change in the primary pollutants in one of the sensitivity tests. As a result, the relative change in modeled ozone concentrations is given by ΔO_3 (X)/O_3.

As shown in Fig. 10, the RIR values are calculated for NO_x, ~~AHC, NHC~~AVOC, NVOC, and CO, respectively. The ~~AHC~~AVOC has the highest RIR (> 1 %/%) in all cities because ozone production is limited to the abundance of VOC in urban areas. In comparison, the RIR of ~~NHC~~NVOC and CO are small (< 0.2 %/%), which demonstrates isoprene and CO are not important ozone precursors in all cities. The only component of NVOC is isoprene, which are on average 0.3 ppbv in Beijing, 0.1 ppbv in Guangzhou, and 0.4 ppbv in Chongqing, but reduce to negligible in Shanghai (below detection limit, Table S3). For NO_x, the RIR values are negative indicating the ozone production is in NO_x-titration regime~~ and thus reducing~~. A slight reduction of NO_x could lead to increase in O_x concentrations within the NO_x-titration regime. It can be explained from the respect of radical budget that the $OH+NO_2$ reaction rate is a dominant part of the radical termination in all cities (Fig. 7). If the radical termination is reduced, the OH-HO_2-RO_2 radical propagation will become more efficient and thus the modeled radical concentrations will increase. One should keep in mind that HONO is scaled to NO_2 in our base model. The reduction in NO_2 also leads to a reduction in HONO, which means less primary radical sources. Therefore, less ozone will be produced from the radical recycling, which compensates for the titration effect partly. We performed further sensitivity study that HONO is free running. The results show that the negative effect becomes more significant compared to the base model scenario (Fig. S9). The reduction of radical termination by $OH+NO_2$ reaction compensates the reduction of radical primary source due to HONO photolysis. Therefore~~S5). In comparison~~, a ~~small~~larger negative effect ~~showed~~shows up in the RIR analysis in the ~~base model run. It is because the HONO photolysis only contributed about 40% to the primary source, smaller than the portion of $OH+NO_2$ to the termination. In another word, if HONO is~~sensitivity test (Fig. S9).

As discussed above, VOCs emission control is critical to ozone pollution reduction. To perform accurate VOC mitigation for O_3 pollution control, the ~~AHC~~AVOC is further split into alkanes, alkenes, and aromatics. As shown in section 3.2, alkenes and aromatics are the dominant VOC groups with respect to OH reactivity. The RIR analysis also showed that reduction in alkenes and aromatics are important for ozone pollution control in these megacities (Fig. 10). Xue et al. (2014) compared the observation in four cities (Beijing, Shanghai, Guangzhou, and Lanzhou) but located in downwind suburban areas. The results showed that ozone increase could be attributed to local ozone production in Shanghai, Guangzhou, and Lanzhou (Xue et al., 2014). Besides, ozone production was in VOC-limited regime in Shanghai and Guangzhou, among which aromatics were the most important contributor. A comparison of two megacities in China (Shanghai and Tianjin) showed that the ozone production is highly variable depending on the VOC speciation at certain NO_x concentrations (Ran et al., 2012). Alkenes were important ozone precursors in Tianjin, while in Shanghai, aromatics dominated the ozone production. Based on a one-year measurement in Nanjing (YRD), the ozone production was in the VOC-limited regime and the Nanjing-Shanghai axis with its city clusters in between was subjected to a regional photochemical pollution (Ding et al., 2013). The regional model (WRF-Chem) also showed ozone production was under strong VOC-limited not only in urban but a larger regional area (Tie et al., 2013). The PRD region has been well studied from field campaigns, emission inventories, and regional modeling (Zhang et al., 2008a;Zheng et al., 2009;Ding et al., 2004). The results showed both urban (Guangzhou) and downwind rural site (Xinken) were under the VOC-limited regime and negative RIR values for NO_x were found (Zhang et al., 2008b). Meanwhile, the ozone-NO_x-VOC sensitivity was found to be VOC-limited in Chongqing and the traffic emission contributed 44% to the VOCs in an urban area (Su et al., 2018;Li et al., 2018b).

4.~~2~~4 Nitrate production potential

Nitric acid is one of the major products generated by the radical system for high NO_x conditions, which is an important precursor of particulate nitrate (NO_3^-). ~~Nitrate~~Recently, nitrate has become a significant portion in particles in Beijing, Shanghai, and Nanjing (YRD) during summertime in China (Li et al., 2018a). The gas phase nitric acid HNO_3 together with ammonium NH_3 form a gas-particle partitioning equilibrium with NH_4NO_3 (R3), which depends on the relative humidity, temperature, and the aerosol contents (Seinfeld and Pandis, 2016).

$$\mathrm{NH_3} + HNO_3 \leftrightarrow NH_4NO_3 \qquad \text{(R3)}$$

The ~~gas-particle partitioning is calculated by~~nitric acid is mainly produced from the ~~aerosol thermodynamic~~reaction between NO and OH which can be derived from the box model~~ (ISORROPIA).~~. The fate of nitric acid depends on the gas-particle partition~~ is assumed to reach equilibrium because~~, deposition and chemical reactions. In general, the time scale of ~~reaching equilibrium is in range of minutes, ~~partitioning is 1-2 orders smaller than those of deposition and chemical production (Morino et al., 2006;Neuman et al., 2003)~~. Therefore, the photochemical produced HNO_3 will deposit on to the aerosol if the ambient NH_3 is sufficient. The nitric acid could also lose via deposition. The decomposition rate is set to be 7 cm s^{-1}, which results in a deposition timescale being 8 hours by assuming the boundary layer height to be 2 km (typical values for summertime). The total ammonia (NH_4TOT) is calculated from an iterative method for each case to reproduce the gas-phase NH_3 concentrations reported by Pan et al. (2018). From the field measurements, the averaged NH_3 concentrations were Beijing: 16.3 $\mu g/m^3$, Shanghai: 14.6 $\mu g/m^3$ (the number is adapted from a close-by city Nanjing), Guangzhou: 5.9 $\mu g/m^3$, and Chongqing: 10.5 $\mu g/m^3$ (the number is adapted from a close-by city Chengdu)~~. Therefore, the photochemical produced nitric acid will deposit on to the aerosol if the ambient NH_3 is sufficient. The deposition rate is about 7 cm s^{-1} (Seinfeld and Pandis, 2016), which results in a deposition timescale being 8 hours if the boundary layer height is 2 km (typical values for summertime). The ammonia concentrations are usually above 10 $\mu g/m^3$ in urban areas in China during summertime (Pan et al., 2018)~~.~~

, which indicates ammonia-rich conditions and sufficient to neutralize nitric acid..

In this study, we use the aerosol thermodynamic model (ISORROPIA) to simulate the nitrate production and the model design is explained in supplement. It's worth noting that such model simulation cannot be quantitatively because some key parameters, e.g. ammonia and nitric acid concentrations were not measured during these campaigns. The discussion below should be considered as a qualitative estimation to show the important feature in determining the particle nitrate production. The modeled nitrate concentration and partitioning in Beijing are shown to illustrate the typical pattern of particulate nitrate formation (Fig. 11a). The total nitrate ~~maximizes~~concentrations maximize in the late afternoon while the particulate nitrate shows a board peak at night, which is mainly driven by the stronger gas-to-particle partitioning due to higher RH. Since deliquesce relative humidity (DRH) of NH_4NO_3 is about 60% in all cases, the partitioning changed dramatically with the relative humidity above DRH (nighttime) and below DRH (daytime). One should note that the nitrate formation from N_2O_5 hydrolysis is not taken into account in this study, which could lead to negative bias in the nitrate production calculation.

To investigate the nitrate concentration dependence on the nitrate production rate and ambient ammonia concentrations, the averaged nitrate concentrations are plotted as a function of daily integrated nitric acid production rate and total ammonium ($NH_4^+{}_{(a)}+NH_{3(g)}$) concentrations. As shown in Fig. 11b, the isopleth diagrams are split into two parts by the dashed line to represent the nitrate- (upper left) and ammonium-sensitive (lower right) regimes. However, the threshold for nitrate- and the ammonium-sensitive regime is not distinct in the small chemical range. Actually, the nitrate concentrations are sensitive to both precursors. The daily integrated nitrate production rate and averaged total ammonium concentrations for each city are denoted by the circles (Fig. 11b). The circles are located above the ridgeline, which means nitrate concentrations are more sensitive to the change of ~~nitrate production rate. In comparison, the averaged nitrate concentrations derived from the time-dependent calculations (as shown in Fig 11a) are 64±7, 27±8, 16±4, and 20±4 $\mu g/m^3$ per day in Beijing, Shanghai, Guangzhou, and Chongqing, respectively. These numbers are consistent with the EKMA plot (Fig. 11b), which indicates the results are reasonable.~~nitric acid production rate. Therefore, this scenario study highlights that the further mitigation of summertime particulate nitrate pollution should aim at the reduction of photochemical nitric acid production. For example, the reduction in NO_x emission could help to reduce the particulate nitrate pollution but may lead to enhancement in ozone pollution (see section 4.3).

~~In the base scenario, the other chemical compositions are set to zero (total SO_4^{2-}, Na^+, and Cl^-). The simplification uncertainty is evaluated by the following sensitivity tests. As shown in Table 2, the NH_4NO_3 concentration and the particulate nitrate to total nitrate ratio $\varepsilon(NO_3^-)$ is calculated for different model scenarios. First, if NH_3 concentrations are changed by a factor of 2, the change to partitioning is relatively small in Beijing because the NH_3 concentrations are high. It's worth noting that NH_4NO_3 concentration is still high even if the NH_3 concentration is reduced by two-fold in Beijing, which highlights the difficulty in particulate nitrate reduction. In contrast, the change almost linearly correlates with the change of NH_3 in Guangzhou during the daytime due to the~~

~~limited amount of NH_3. The role of other anions and cations is investigated by setting the SO_4^{2-} and Na^+ to be 10 µg/m³, respectively. Since SO_4^{2-} reacts with NH_4^+ and thus competes with the formation of NH_4NO_3. The NH_4NO_3 formation will be limited if NH_3 is not sufficient given the NH_3 to tend to react with SO_4^{2-} before NO_3^-. The nitrate concentrations decrease by 1-3 µg/m³ when SO_4^{2-} is fixed in all cities to be 10 µg/m³ during day and night (Table 2). In contrast, additional cations can neutralize more nitrates and enhance the gas-to-particle partitioning. For example, if 10 µg/m³ of Na^+ is added, stronger nitrate production is found (Table 2). It is caused by two kinds of effect. First, the stronger partitioning enhances the particulate nitrate directly. Second, the total nitrate loss is reduced by less $HNO_{3(g)}$ deposition because more nitrate remains in the particle phase.~~

4.~~3~~5 Atmospheric oxidation capacity and secondary pollution formation

Atmospheric oxidation capacity is mainly contributed by OH radical which dominates the chemical removal of trace gases (e.g. CO, NO_2, VOCs). The OH reactions convert primary pollutants to oxidized products (e.g. CO_2, HNO_3, OVOCs). As shown in Fig. 12, the daytime averaged OH oxidation rate is up to 10 ppbv/h in Beijing, indicating strong oxidation capacity (daily integrated oxidation rate > 100 ppbv). The OH oxidation rate is comparable in Shanghai and Chongqing (~5 ppbv/h) and reduces to 4 ppbv/h in Guangzhou. In this study, the OH oxidation rate correlates with the strength of primary radical sources $P(RO_x)$. Actually, the ratio between the radical recycling rate and the primary production rate indicates the efficiency of radical propagation (E6), also known as the radical chain length.

$$\mathrm{ChL} = (k_{VOC} + k_{CO}) \times [\mathrm{OH}]/\mathrm{P(RO_x)} \tag{E6}$$

where k_{VOC} and k_{CO} represent the reactivity of VOC and CO versus OH radical, respectively.

The radical chain length is on average 2.9 ± 0.3 for all cases, which is consistent with the results (3-5) derived from radical observation in urban areas (Kanaya et al., 2008;Ren et al., 2006;Emmerson et al., 2005).

As shown in section 3.3.2, $P(RO_x)$ is highly correlated with $j(O^1D)$ because photolysis reactions dominate the RO_x primary sources. An exception happens in Guangzhou that $P(RO_x)$ decrease by a factor of 2 compared to Beijing although $j(O^1D)$ is reduced by a factor of 3. It is because alkenes ozonolysis reactions increase to 0.7 ppbv/h in Guangzhou (0.2-0.3 ppbv/h for other cities) and contribute nearly half of the primary source. The reduction of $P(RO_x)$ in Guangzhou is partly compensated.

More than half of the OH oxidation rate was contributed by the reaction with VOC that produce less volatile species (OVOCs) (Fig. 12). Therefore, these oxidized compounds have the potential to contribute to the particle formation due to their low volatility (Odum et al., 1997). Besides, the oxidation of NO_2 produces HNO_3, which can contribute to the particle formation given the relatively high ambient NH_3 concentrations (see in section 4.2).

O_3 is another important secondary pollutants generated from the OH-HO_2-RO_2 radical system. The averaged $P(O_3)$ is consistent with the OH oxidation rate in four cities (Fig. 12). The ratio between ozone production and radical primary production rate is used to evaluate the ozone production efficiency (OPE). In this study, the OPE is highest in Chongqing (3.6 on average) due to the relative high VOC/NO_x ratio. In contrast, OPE is only 2.2 in Guangzhou and increases to 3.4 and 3.1 in Beijing and Shanghai. In comparison, the OPE was found to be in the range of 3 to 7 in other cities (Kleinman et al., 2002;Lei et al., 2008). The OPE determined in this study is in the low range compared to other cities in the US, which is due to the suppression of high NO_x conditions. Since OPE generally increases with time when a plume is transported and diluted (Kleinman et al., 2002), the ozone production becomes more efficient in the suburban areas of the megacities.

Finally, the radical inner recycling rate is on average 4-5 times larger than that of radical initiation (termination), which demonstrates that the secondary pollutant formation rate (e.g. ozone, nitric acid) is enhanced by the efficient radical recycling.

5. Summary and conclusion

Secondary pollution has been increasing in the last decade in Chinese cities despite the reduction of primary pollution. Ozone and fine particle precursors (e.g. H_2SO_4, HNO_3, and ELVOCs) are generated from the radical reactions. Therefore, atmospheric oxidation capacity is the core of secondary pollution formation. In this study, we present the observation of the radical precursors at four Chinese megacities during photochemical polluted seasons, namely Beijing (July), ~~Shang~~Shanghai (August), Guangzhou (October), and Chongqing (August). A box model is used to simulate OH, HO_2 and RO_2 concentrations. The key processes are elucidated with explicit radical budget analysis. The formation mechanism of secondary pollutants (ozone, particle precursors) is investigated with the chemical model. The major findings for this study are shown in the following:

1) The metric of OH reactivity is used to demonstrate the air pollutants burden. The modeled OH reactivity show typical diurnal profiles with a maximum in the morning and minimum in the afternoon. The OH reactivity is highest in Guangzhou (20-30 s^{-1}), followed by Beijing and Chongqing (15-25 s^{-1}), and smallest in Shanghai (<15 s^{-1}). More than half of the OH reactivities are contributed by inorganic species, i.e. CO and NO_x. The measured AVOCs contribute to the total OH reactivity from 14% to 26%. In Guangzhou, the contribution and absolute reactivity (6 s^{-1} compared to 2~3 s^{-1} in other cities) are highest due to the large contribution from aromatics. ~~The shares of different VOCs groups are comparable with slightly different contribution between alkanes and alkenes (in total make up 40% of the VOC reactivity except in Guangzhou).~~The most important OH reactants VOC is propene among all cities.
2) Modeled OH concentrations show distinct diurnal variation. The OH mean diurnal profile maximum is largest in Beijing and Shanghai (7×10^6 cm^{-3}) and decreases to 4×10^6 cm^{-3} in Chongqing and 2×10^6 cm^{-3} in Guangzhou. The modeled OH concentrations are correlated with the photolysis frequencies ($R^2 > 0.7$) with a correlation slope to 2.0×10^{11} cm^{-3} s^{-1} (3.0×10^{11} cm^{-3} s^{-1} in Shanghai). The peroxy radicals concentrations are highest in Chongqing with a diurnal maximum of 5×10^8 cm^{-3} for HO_2 and 7×10^8 cm^{-3} for RO_2 due to the relatively high VOCs/NO_x ratio.
3) The dominant radical sources are photolysis reactions, including HONO, O_3, HCHO and other carbonyl compounds, among which photolysis of HONO and HCHO make up nearly half of the primary sources. The mean diurnal maximum is largest in Beijing (5 ppbv/h), followed by Shanghai (4.6 ppbv/h) and Chongqing (4.3 ppbv/h), and is smallest in Guangzhou (3.2 ppbv/h) due to the later observation period in a year. However, the alkene ozonolysis contributes significantly to the radical sources in Guangzhou (43% of the total primary source for daytime conditions).
4) The daily integrated local ozone production rate is largest in Beijing (136 ppbv) and reduced to 92, 40, 105 ppbv in Shanghai, Guangzhou, and Chongqing, respectively. The measurement site represents city center conditions, where ozone precursors are fresh emitted. With the advection of fresh-emitted air mass, NO_x and VOCs undergo efficient photochemical processes producing a large amount of ozone and transmitted to downwind regions. The outflow of O_x is identified in Beijing, Shanghai, and Chongqing during the afternoon and in Guangzhou after sunset.
5) Ozone production is in VOC limited in all the cities presented because the L_N/Q ratio is greater than 0.5. Besides, we find that the RIR values of ~~AHC~~AVOC are highest in all cities compared to CO, NO_x, and isoprene. The speciation shows that alkanes and alkenes are a major contributor to total OH reactivity except in Guangzhou. In the sense of ozone formation potential, aromatics become dominant species due to their large carbon numbers and thus high MIR value. In Guangzhou, aromatics contribute up to 70% of the share of OFPs, followed by Shanghai (55%), Beijing (43%), and Chongqing (42%). In comparison, alkanes are the major contributor to the mixing ratios but had limited impact on the ozone formation and radical chemistry. To avoid the bias in the understanding of photochemistry process, it's more proper to use the concept of OH reactivity.
6) The coexistence of high OH and NO_2 concentrations resulted in fast nitric acid production rate. The partitioning between HNO_3 and NO_3^- is analyzed using a thermal dynamic model (ISORROPIA2). In the presence of abundant ammonium, the

photochemical produced HNO_3 can partition to aerosol phase efficiently under high RH conditions. ~~The daily integrated nitrate production rates are 64±7, 27±8, 16±4, and 20±4 μg/m³ per day in Beijing, Shanghai, Guangzhou, and Chongqing, respectively. This study demonstrates that active radical chemistry could contribute to the particle pollution.~~

Author contribution

YZ, KL organized the field campaign. KL and YZ designed the experiments. KL, and ZT analyzed the data. ZT wrote the manuscript. All authors contributed to measurements, discussing results, and commenting on the manuscript.

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Table 1 Overview of the measurement sites.

Site	Location	Observation period	1h O_3 maximum [ppbv]
Beijing	116.42 °E, 39.92 °N	Jul. 02 — Jul. 19 2014	110
Shanghai	121.54 °E, 31.12 °N	Aug.21 —Sep. 02 2016	123
Guangzhou	113.33 °E, 23.10 °N	Oct. 23 —Oct. 31 2015	100
Chongqing	106.57 °E, 29.64 °N	Aug. 27 — Sep. 04 2015	79

~~**Table 2 Equilibrium Model sensitivity summary for NH_4NO_3 mass concentration and particulate nitrate to total nitrate ratio $\varepsilon(NO_3^-)$ during daytime (06:00 – 18:00) and nighttime (00:00 – 06:00, 18:00 – 24:00).**~~

Table 2 The top 10 VOCs contribution to OH reactivity during the four campaigns.

VOCs	Beijing	Shanghai	Guangzhou	Chongqing
PROPENE	0.40	0.61	0.40	0.52
ISOPRENE	0.64	0.00	0.31	0.92
ETHANE	0.58	0.29	0.24	0.59
ETHENE	0.41	0.17	0.29	0.73
M,P-XYLENE	0.29	0.27	0.74	0.31
TOLUENE	0.18	0.12	0.73	0.15
STYRENE	0.06	0.28	0.26	0.16
TRANS-2-BUTENE	0.17	0.00	0.31	0.26
O-XYLENE	0.06	0.08	0.35	0.10
1,2,4-TRIMETHYLBENZENE	0.08	0.13	0.16	0.17

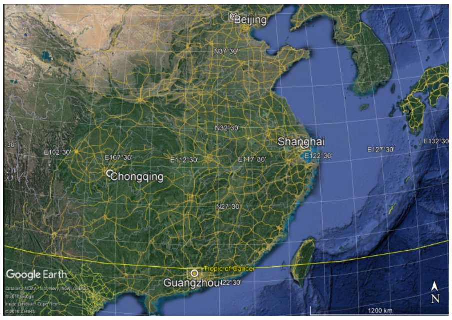
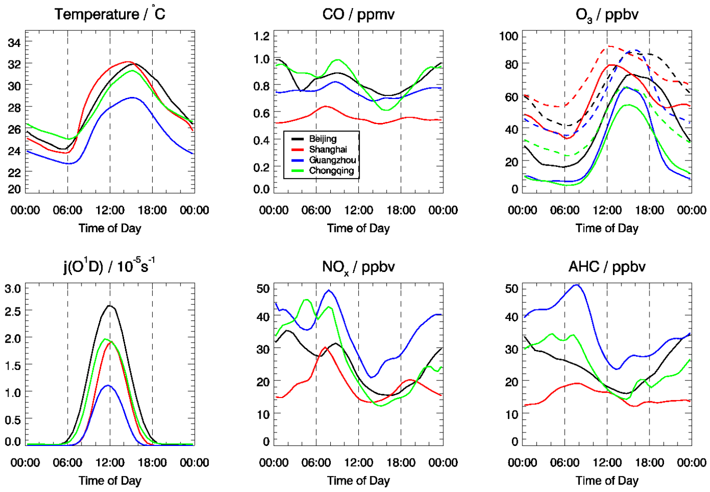


Figure 1. The location of the four measurement sites in Chinese megacities.



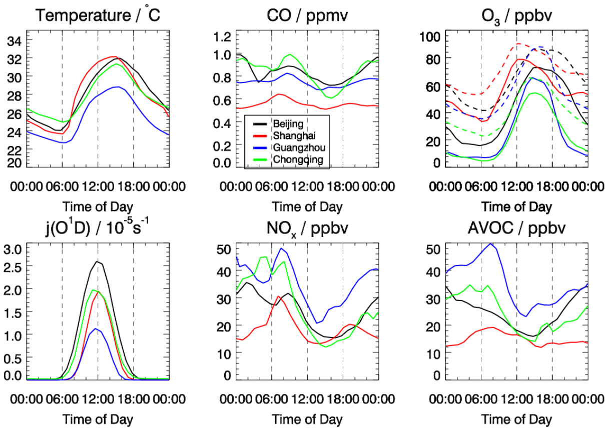


Figure 2. Mean diurnal variation of measured temperature, CO, O_3, $j(O^1D)$, NO_x and Anthropogenic Volatile Organic Compounds (~~AHC~~AVOC) in four field studies. O_x is denoted in the same panel as O_3 with dashed lines.

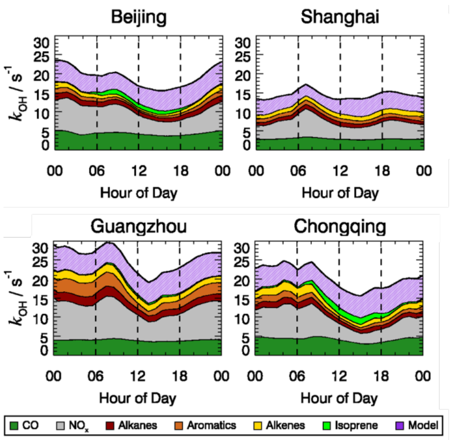


Figure 3. Mean diurnal profile of contributions from all measured species for OH reactivity in Beijing, Shanghai, Guangzhou, and ~~Chengdu~~Chongqing. The filled areas represent different atmospheric constituents. The model denotes the sum of model generated species such as formaldehyde, acetaldehyde.

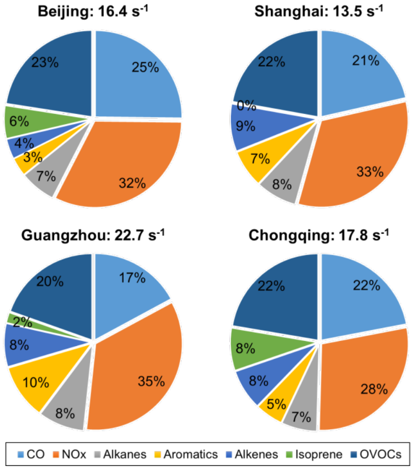
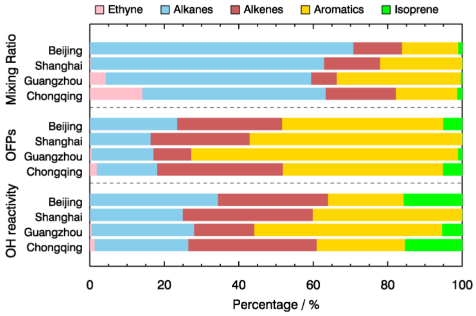
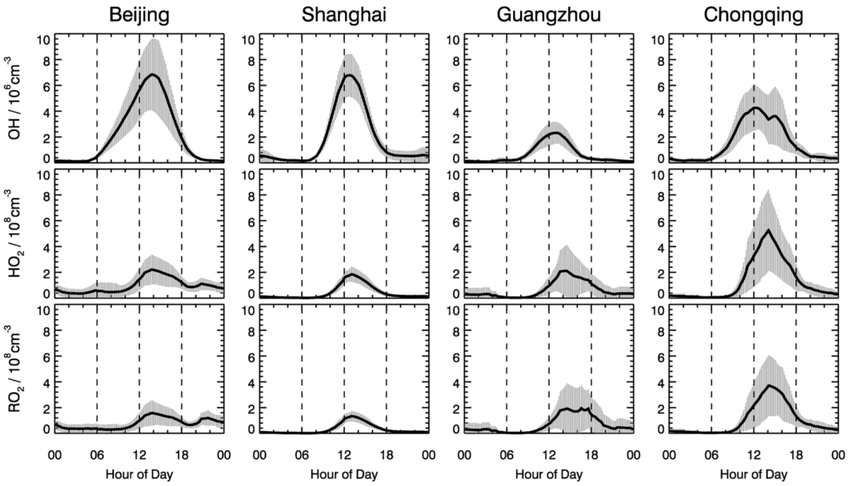


Figure 4. Contributions of different atmospheric constituents to OH reactivity in Beijing, Shanghai, Guangzhou, and Chongqing. The OVOCs contributions are simulated by a box model.



~~Figure 5. The group compositions (mixing ratios) in percentages for VOCs as well as their shares in OFPs and OH reactivity for four cities.~~



~~Figure 6.~~.

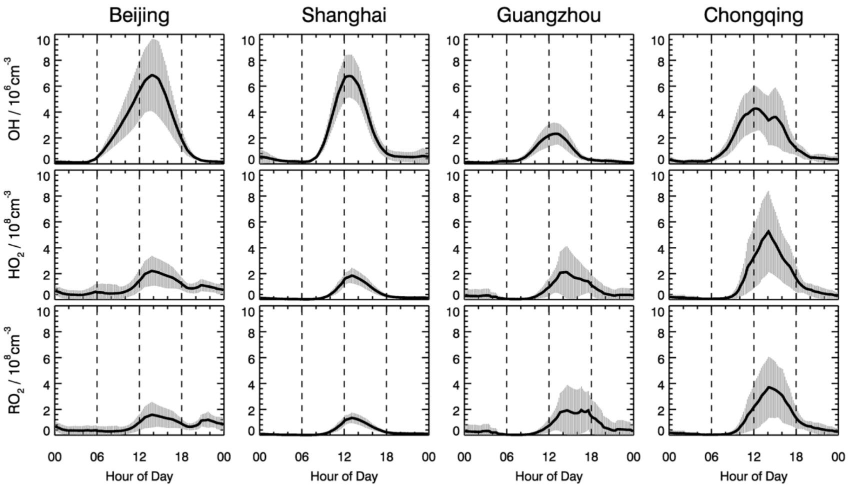


Figure 5. Mean diurnal profiles of modeled OH, HO_2, RO_2 concentrations in four measurement sites. The vertical bars denote the daily variability of model ~~calculations.~~calculated radical concentrations.

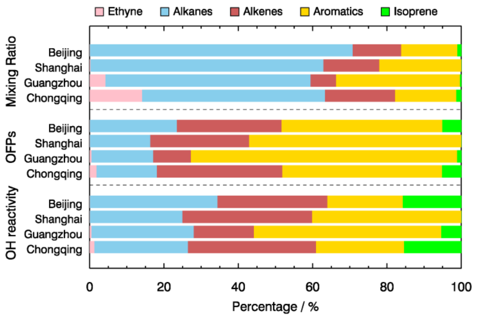


Figure 6. The group compositions (mixing ratios) in percentages for primary VOCs as well as their shares in OFPs and OH reactivity for four cities

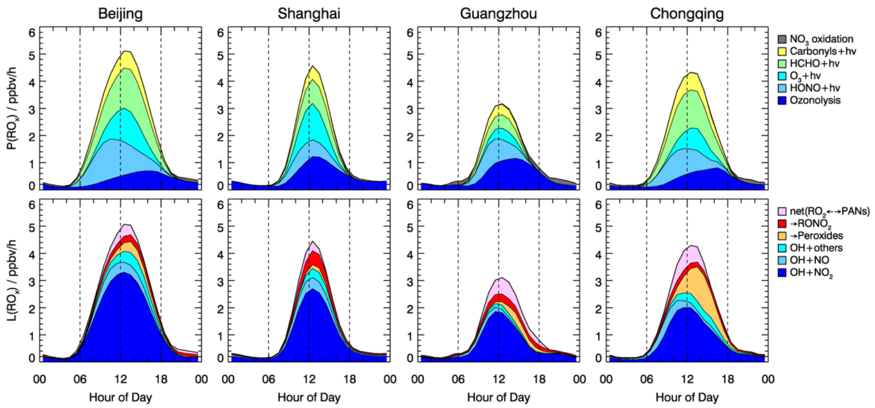
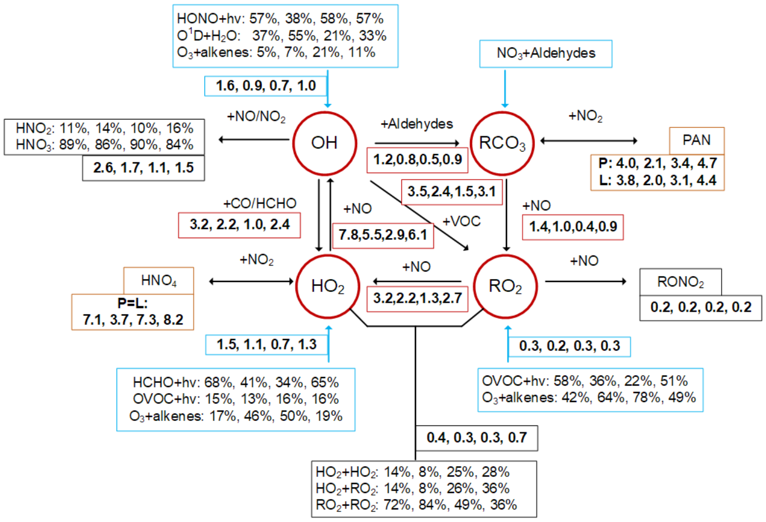


Figure 7. Hourly averaged primary sources and sinks of RO$_x$ radicals derived from model calculations in four measurement sites.



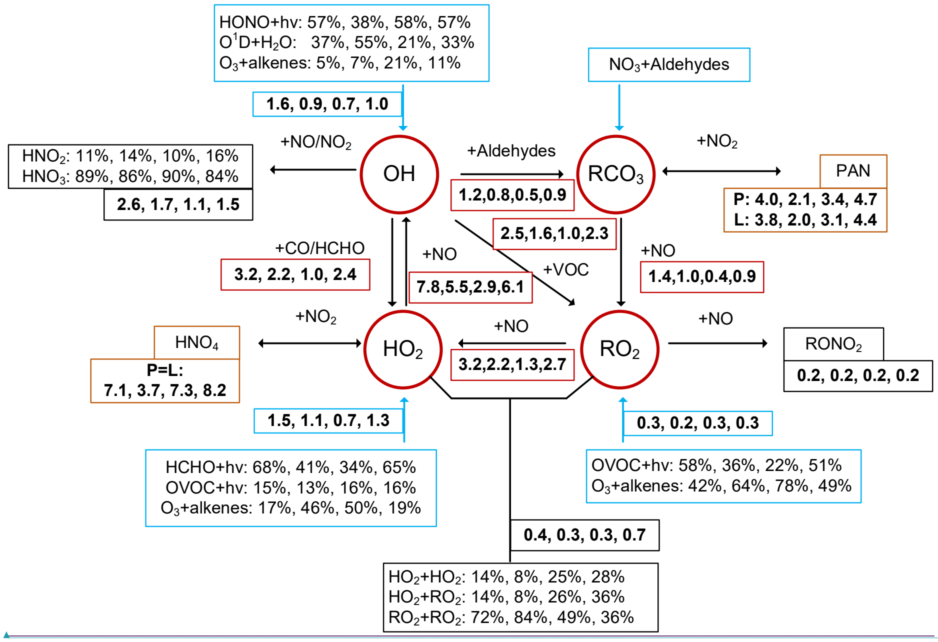


Figure 8. Comparison of OH-HO$_2$-RO$_2$ radical budget in four cities for daytime conditions (06:00-18:00). The numbers are sorted in the order of Beijing, Shanghai, Guangzhou, and Chongqing from left to right. Blue boxes denote radical primary sources, black boxes denote radical termination, red boxes denote radical propagation, and yellow boxes denote equilibrium between radicals and reservoir species.

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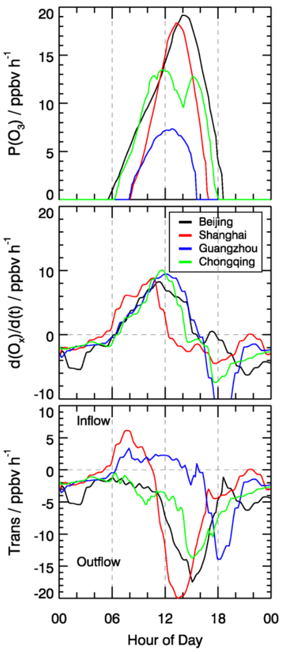
$P(O_3)$ / ppbv h^{-1}
20
15
10
5
0
$d(O_x)/d(t)$ / ppbv h^{-1}
20
10
0
-10
Beijing
Shanghai
Guangzhou
Chongqing
Trans / ppbv h^{-1}
10
5
0
-5
-10
-15
-20
Inflow
Outflow
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06
12
18
00
Hour of Day

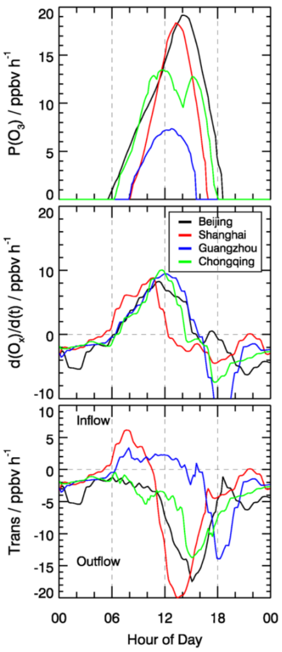
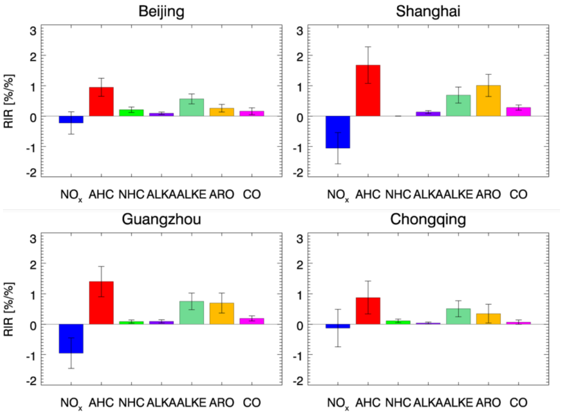


Figure 9. In situ ozone budget analysis at four cities. The upper panel denotes the local ozone production rate P(O$_3$) derived from model calculation. The middle panel denotes the derivatives of observed O$_x$ concentrations d(O$_x$)/d(t). The bottom panel denotes the difference between P(O$_3$) and d(O$_x$)/d(t), which indicate the role of local chemical production on transportation (see text).



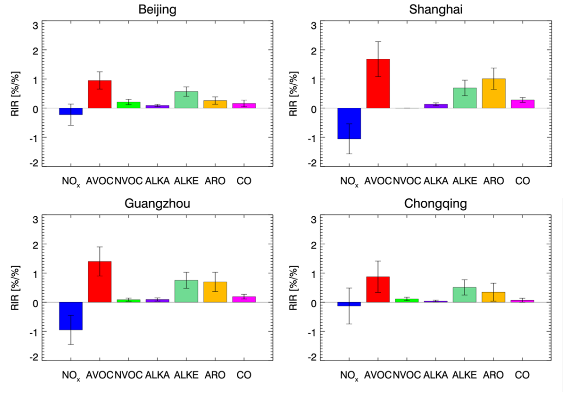


Figure 10. The RIR analysis for NO$_x$, ~~AHC~~AVOC, CO and ~~NHC~~NVOC (natural volatile organic compounds, in this study only isoprene is considered) at four sites.

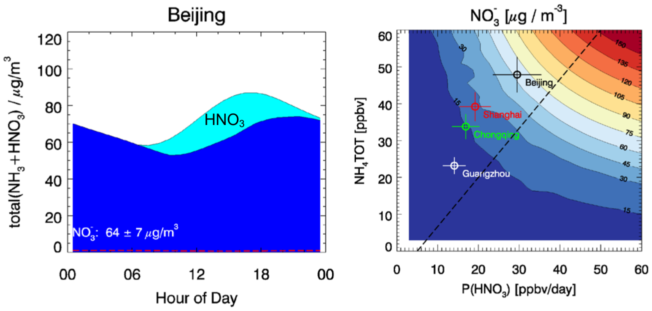


Figure 11. Modelled nitrate production from gas-phase oxidation. (a) The mean diurnal profile of modelled total nitrate concentration and its gas-particle partitioning. (b) Functional dependence of particulate nitrate concentrations on daily integrated nitrate production rate and total ammonium concentrations.

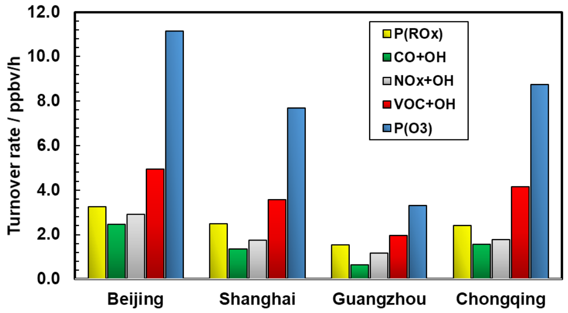


Figure 12 Inter-comparison of atmospheric oxidation rate for four megacities.