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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric oxidation capacity in Chinese megacities during photochemical polluted season: radical budget and secondary pollutants formation" *by* Zhaofeng Tan et al.

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.

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.

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

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.

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.

Specific Comments:

Title: Atmospheric oxidation capacity in four Chinese megacities. . .

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

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

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

P2, L11: the role of. . .

P3, L7: are located. . .

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

P3, L21: Instrumentation

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.

P3, L29-30: rephrase this sentence.

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

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

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

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

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

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.

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

P10, L34: change decomposition to deposition

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

P12, L25: change Shang to Shanghai

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

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

Figure 6: what does "variability" stand for?

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