

## ***Interactive comment on “Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes” by L. K. Xue et al.***

**Anonymous Referee #3**

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General comment and recommendation:

This study investigated ozone chemistry at four cities in China. Measurements from 4 field observation campaigns were analyzed using an OBM model. The value of a dataset consisting of in-situ measurements from 4 field campaigns is significant. However, it seems to me that this work is merely a collection of four independent case studies. The authors did not make an in-depth cross-case analysis and, thereby, I cannot see how a case relevant to the others. Such a “report” could be useful to formulation of air quality control strategy in China; however, I did not see scientific merits to support it published as an ACP paper. Furthermore, there are indeed some

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major flaws in the data analysis and interpretation as listed in the followings. Thus I recommend reject this submission.

Specific comments:

1. The contribution of urban plumes to ozone pollution in downwind areas was evaluated using a simple equation,  $R_{\text{trans}} = R_{\text{meas}} - R_{\text{chem}}$  (Sec 3.2). Note that the term of in-situ photochemical ozone production (EQ1) is actually defined as the oxidation of NO by XO<sub>2</sub>, which means production of NO<sub>2</sub> and in turn all the products relevant to the “O” from NO<sub>2</sub> photolysis (usually defined as total oxidant). This is why the loss term of ozone (EQ2) including not only ozone but also other major oxidants. In the calculation of  $R_{\text{trans}}$ ,  $R_{\text{meas}}$  is the changes in ozone, whereas  $R_{\text{chem}}$  is theoretically defined on “total oxidant”. Thus the calculated  $R_{\text{trans}}$  cannot be a measure of transport effect because it includes many other factors relevant to chemical equilibrium among oxidants, titration reaction of O<sub>3</sub> and NO for instance. In this context, all the conclusions drawn from  $R_{\text{trans}}$  analysis could be false, or true but based on wrong inferences.
2. Moreover, it was mentioned that “the atmospheric mixing was also included here”. However, it’s unclear throughout the paper how the atmospheric dynamics was considered in this work. Dynamics of mixing layer could be one of the major mechanisms responsible for the drastic changes in  $R_{\text{trans}}$ , as shown in Fig 5. (There was no discussion explaining those spikes or sudden changes in  $R_{\text{trans}}$  in the maintext.)
3. The sensitivity of ozone to precursors in three of the four cases was discussed in Sec 3.3. Why did you drop out the case of Beijing?
4. At the end of Sec 3.3, the authors claim that this study is a good effort as a cross-region comparative study. However, again, I did not find any real “cross-region” analysis in addition to lumping four cases in one article.
5. Heterogeneous reactions were discussed in Sec 3.4. However, as the paper entitled as a study of four cities, only a 1-day case of Shanghai was discussed for N<sub>2</sub>O<sub>5</sub> and

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HO<sub>2</sub> chemistry, and another 1-day case of Guangzhou for HONO reactions. I disagree that the two cases can be representatives of the complicated atmospheric chemistry in urban areas.

6. The work of Sec 3.4 is to investigate the responses of ozone production to N<sub>2</sub>O<sub>5</sub> hydrolysis, HO<sub>2</sub> uptake by aerosols, and HONO from surface reactions of NO<sub>2</sub>, respectively. In a model study, adding a source or sink reaction will certainly result in a corresponding outcome and the scientific question is how significant the outcome change due to the inclusion of a new factor. In all the three case studies presented here, the ozone production changed by ~10% only as compared to the respective control runs. The authors claimed that the changes were significant. However, I think the conclusions cannot be drawn before the uncertainties associated to the simulations are carefully evaluated.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27243, 2013.

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