

**Referee #2:**

The manuscript attempts to investigate the factors controlling the urban ozone (O<sub>3</sub>) pollution during a specific period using the WRF-Chem model. The topic is of interest, but generally the manuscript is not well written and further English polishing is imperative. There are several fatal factors hindering publication of the manuscript at present.

**Reply:** we thank the reviewer for the comprehensive comments to improve the manuscript. The language has been polished by professional editor (shown below) and all the comments have been addressed in detail.



**English editing certificate**

1. In the abstract, the authors clarified that they found a unique mechanism to modulate the high O<sub>3</sub> formation. 1) Prevailing northerly winds convey O<sub>3</sub> precursors (not “emission sources”) to the YRD region; 2) The vertical diffusion and the enhanced process of local chemical generation cause the

growth of near-surface O<sub>3</sub> in Hangzhou. What is the role of the trans-boundary transport of O<sub>3</sub> precursors in the O<sub>3</sub> formation mechanism suggested by authors?

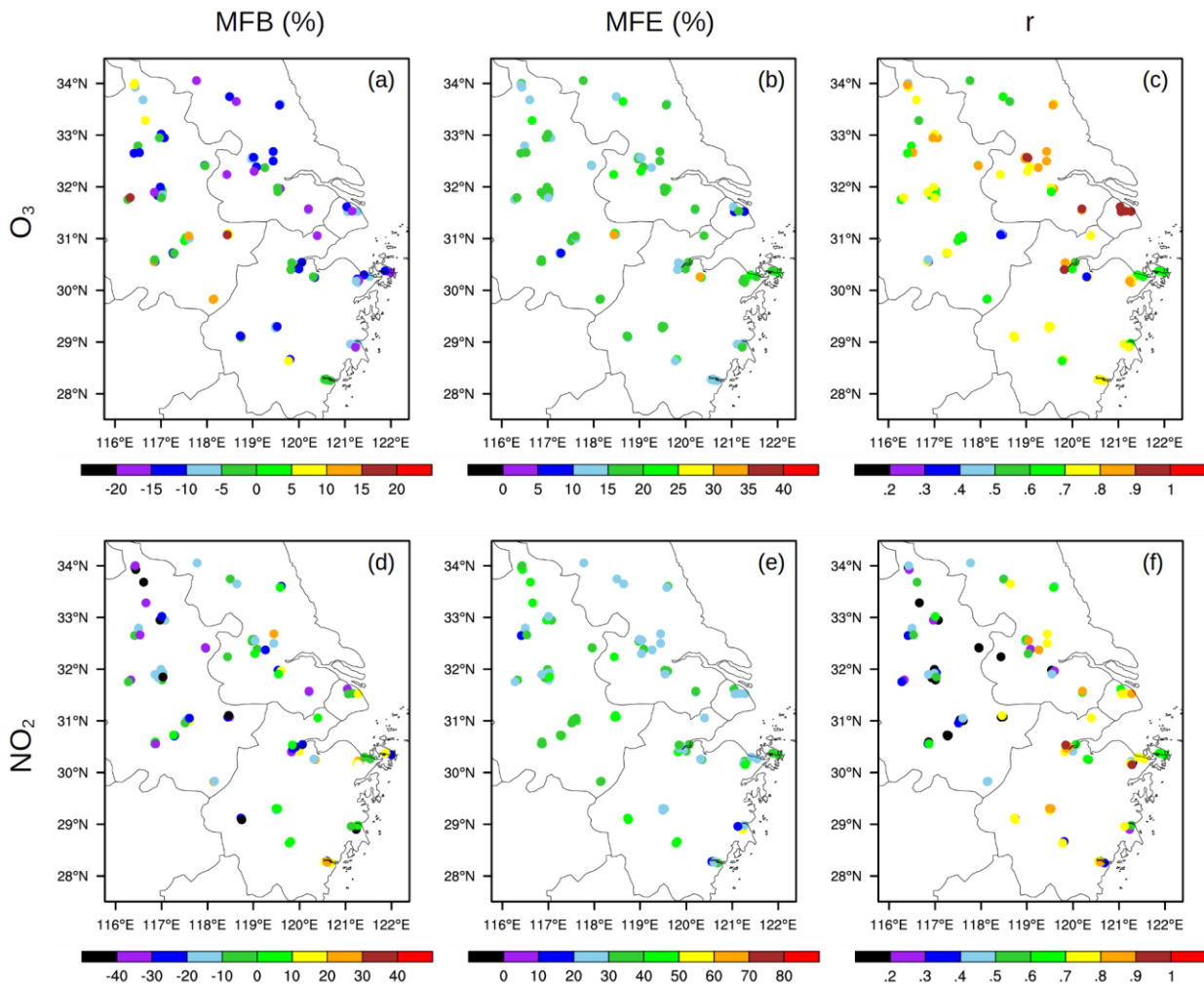
**Reply:** “emission sources” has been replaced as “O<sub>3</sub> precursors”.

To address the reviewer’s concern regarding the role of trans-boundary transport of O<sub>3</sub> precursors in the O<sub>3</sub> formation, a few numerical experiments were designed to quantify the impact from the upwind areas. The dominant wind directions are northerly based on meteorological conditions (not shown), therefore, the emissions in Shanghai (Northeast of Hangzhou), Jiangsu (North of Hangzhou) and Anhui (northwest of Hangzhou) were zeroed out, separately, to elucidate their individual impact on the ozone concentration in Hangzhou. During August 24-September 6 2016, the contribution from Shanghai, Jiangsu and Anhui to ozone concentration in Hangzhou is on average (maximum) of 3.0% (9.2%), 7.0% (19.0%) and 3.0% (18.7%), respectively, illustrating nontrivial contributions from the neighboring provinces. This information has been added to the section 3.4 (lines 301-309) of the revised manuscript.

2) About the model validation. The authors need to provide the horizontal distributions of O<sub>3</sub>, NO<sub>2</sub>, and PM<sub>2.5</sub> with the observations at monitoring sites in the simulation domain. The China’s MEE has released hourly observations of air pollutants since 2013, including PM<sub>2.5</sub>, PM<sub>10</sub>, O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub>, which can be used to validate the model performance.

**Reply:** We have provided the model validation from the perspective of horizontal distributions. Since ozone is the major focus in this study, the evaluation focuses on O<sub>3</sub> and its major precursor such as NO<sub>2</sub>. The discussions of Fig. S1 have added in the revised manuscript (lines 198-202).

The spatial distributions of MFB and MFE for ozone and NO<sub>2</sub> at the 96 observational sites over YRD region was shown in Fig. S1, illustrating reasonable performance by showing most of the sites with MFB/MFE meeting the benchmarks (15%/35%) and correlation coefficient of 0.7 or higher.



**Fig. S1.** Comparison of modeled air pollutants concentrations against measurements in 96 monitoring sites during August 24–September 6, 2016: Mean fractional bias (MFB), mean fractional error (MFE) and Pearson's correlation coefficient ( $r$ ) of  $O_3$  (a–c) and  $NO_2$  (d–f), respectively.

3) About discussions. In the urban region,  $O_3$  is formed as a result of photochemical reactions involving volatile organic compounds (VOCs) and nitrogen oxide ( $NO_x$ ) in the presence of sunlight. However, in the discussion, the  $O_3$  formation in the mechanism suggested by authors does not seem to be associated with VOCs. In addition, the authors clarified: “Oxidation reactions of VOCs, under the present of CO, provide alternative oxidants (i.e.,  $HO_2$  and  $RO_2$ ) that efficiently convert NO to  $NO_2$ . This conversion enriches the reactants to  $O_3$  photochemical generation while suppressing titration consumption, resulting in the accumulation of  $O_3$ .”. This is really confusing. Why does CO facilitate VOCs oxidation? Why does the  $O_3$  formation suppress titration?

**Reply:** We thank the reviewer for clarifying the mechanism of O<sub>3</sub> formation. The reviewer is correct that O<sub>3</sub> is formed as a result of photochemical reactions involving volatile organic compounds (VOCs) and nitrogen oxide (NO<sub>x</sub>) in the presence of sunlight. The reason we emphasize NO<sub>x</sub> more is taking into account of NO<sub>x</sub> limited regime that usually exists in megacities. The discussion of CO was mainly due to the consideration of the following reactions:  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ ;  $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$ . The original statement of “This conversion enriches the reactants to O<sub>3</sub> photochemical generation while suppressing titration consumption” indicates the conversion of NO to NO<sub>2</sub> suppresses the titration not the O<sub>3</sub> formation. To make it clear, we rephrase the statement in the revised manuscript (last paragraph of the discussions, lines 370-373), which is also shown below.

Chemical generation of O<sub>3</sub> is the net effect of photochemical generation and titration consumption. VOC oxidation (Jenkin et al., 1997; Sillman, 1999) in photochemical reactions provides critical oxidants (i.e., RO<sub>2</sub>) that efficiently convert NO to NO<sub>2</sub>, resulting in further accumulation of O<sub>3</sub> (Wang et al., 2017).

Reference:

Jenkin, M. E., Saunders, S. M. and Pilling, M. J., 1997. The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, *Atmos. Environ.*, 31(1), 81–104, doi:10.1016/S1352-2310(96)00105-7

Sillman, S.: The relation between ozone, NO(x) and hydrocarbons in urban and polluted rural environments, *Atmos. Environ.*, 33(12), 1821–1845, doi:10.1016/S1352-2310(98)00345-8, 1999.

Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L. and Zhang, L.: Ozone pollution in China: A review of concentrations, meteorological influences, chemical precursors, and effects, *Sci. Total Environ.*, 575, 1582–1596, doi:10.1016/j.scitotenv.2016.10.081, 2017.

4) Fig. 4, what causes the O<sub>3</sub> simulation biases during nighttime? Fig. 7 is too busy and needs to be

revised.

**Reply:** The underestimations of O<sub>3</sub> during nighttime mainly occurs in the upper levels, which are partly due to the unconsidered upper-air emission sources such as lightning-induced NO<sub>x</sub> (Schumann and Huntrieser, 2007) and aircraft-induced NO<sub>x</sub> (Gauss et al., 2006).

The original Fig. 7 has been revised to be more clear and compact, shown in the revised manuscript.

#### References:

Schumann, U., Huntrieser, H., 2007. The global lightning-induced nitrogen oxides source. *Atmos. Chem. Phys.*

*Atmos. Chem. Phys.* 7, 3823–3907. <https://doi.org/10.5194/acpd-7-2623-2007>

Gauss, M., Isaksen, I.S.A., Lee, D.S., Søvde, O.A., 2006. Impact of aircraft NO<sub>x</sub> emissions on the atmosphere -

tradeoffs to reduce the impact. *Atmos. Chem. Phys.* 6, 1529–1548. <https://doi.org/10.5194/acp-6-1529-2006>