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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone formation under low solar radiation in eastern China" *by* Xuexi Tie et al.

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Responses to Reviewers:

Reviewer 2:

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following their suggestions as is described below.

This work tried to explain the measured co-occurrence of high PM2.5 and O3 concentrations. The authors report that the high daytime HONO concentrations could be photo-dissociated to be OH radicals, which enhance the photochemical production of O3, although depressed solar radiation under heavy PM2.5 pollutions. It is an interesting scientific issues. However, the data and method in the manuscript do not support

such a conclusion very well at this stage.

My major concerns are listed as follows:

(1) The authors mixed observations from Shanghai and Beijing to create an illusion. There are no observations to show high PM2.5-O3-HONO concentrations both at Shanghai and at Beijing. I just see high PM2.5-O3 during Oct.5-6, 2015 in Beijing and high PM2.5-HONO during September, 2009 in Shanghai.

Thanks for pointing out this issue. The reason we chose the data by the following reasons. (1) Because the co-occurrence between O3 and PM2.5 are not always happened, it happens only in some episodes, especially in spring and fall. In winter, O3 and PM2.5 are actually anti-correlated due to low solar radiation (This also can see in Fig. 2 of the paper). It occurs under the following condition, (a) under cloud-free condition, (b) solar radiation is not too low, (c) during heavy aerosol pollutions in large cities in eastern China. Due to these limitations, it requires continuously measurements of O3 and PM2.5, and HONO concentrations. Recently, there are some continuously measurements of PM2.5, and O3 concentrations released by EPA of China. However, HONO measurements are not continuously measured, and we cannot find the HONO data with the period of co-occurrence between O3 and PM2.5. However, we do find some HONO measurements, which all shows that in all major Chinese cities in either fall or winter (Shanghai, Beijing, and Xian), the HONO concentrations were significant higher than other regions (see attached Fig-A1; Now in Fig. 8 of revised paper). For example, HONO concentrations reached highest in night, ranging from 1 to 2.5 ppbv in the morning at 6-9am. In daytime, the concentrations were lowest (ranging from 0.3 to 1.0 ppbv at12-18pm), but the concentrations were still significant higher than other regions, which could have significant effect on the production of OH radicals in daytime. As a result, we think that the high HONO is a common event in large cities in eastern China, especially in daytime. This high daytime high HONO is supported by the measurements in previous studies (Zhang et al. 2016; Huang et al. 2017). In this study, we make an assumption that the co-occurrence between O3 and PM2.5 occurred under high HONO concentrations. From Fig.-A1, we also note that using this assumption may result in some uncertainties in estimating the effect of HONO on OH. For example, using the measured HONO in Xi'an and Beijing could produce 1-2 times higher OH production by photolysis of HONO than the result by using the measured data from Shanghai. In this case, we use the measured HONO from Shanghai to avoid the over estimate of the HONO effect, which can be considered as a low-limit estimation. The above statements are added in the revised paper.

(2) Is the observed co-occurrence of high PM2.5 and O3 concentrations of statistical significance? Are the authors sure it's (measurements during Oct.5-6) not a special case?

The co-occurrence of high PM2.5 and O3 concentrations was occurred in several cases in the past years. The attached Fig.-A2 shows some examples. Because it happened under some special conditions (see the reply in question 1), it most occurred in spring and fall seasons. (3) Could the authors make an effort to exclude the effects of precursor emissions (e.g., being sure that the VOCs/NOx ratios are not more beneficial for ozone production during Oct.5-6 than other days) and meteorological conditions (e.g., temperature and relative humidity; under low humidity, although the PM2.5 concentration is high, the solar radiation would not be depressed much)? Moreover, there are no observations show the solar radiation are exactly depressed during Oct.5-6 in Beijing or September in Shanghai?

Thanks for the valuable comments. We tried to find the available data, which is available during the period of Oct. 5 to 6, 2015. We do find some interesting data, which could answer the some comments of the reviewer. The additional data also helps to improve the quality of the paper. Fig.-A3 (now Fig. 5 in the revised paper) shows the cloud conditions in Beijing. During the period, there was close to the cloud free conditionïijŇbut there was a very heavy aerosol layer. Fig.-A4 shows the relative humidity (RH) conditions. It shows that the RH (%) was generally higher than 60%, with a maximum of 95% during the period. As a result, the high aerosol concentrations companied

by high RH produced important effects on solar radiation. As shown in Fig.-A5 (now Fig. 6 in revised paper), the daytime averaged solar radiation was significantly reduced (about 40% reduction in Oct. 5-6 compared with the value of Oct. 8). We thanks the comments by the reviewer, these addition (figures and text) can significant enhance the quality of the paper.

(4) If the authors insist the high PM2.5-O3-HONO mechanism, could this possible new mechanism be added to the WRF-Chem model for verification?

Adding the high PM2.5-O3-HONO mechanism is a very challenge work, and could be another scientific work in the future. The major difficulty is that the causes (surface emissions or chemical transformations?) for the high HONO concentrations in large Chinese cities are not clearly understood. This could be a very interesting work in the future.

(5) Discussion in sect.3.3: the conclusion (solar radiation in winter reaches a threshold level to prevent the OH chemical production, even by including the HONO production term) came too hastily without no direct evidence.

Thanks for the comment. We agree with the reviewer that this conclusion is not very certain, and we re-write these sentences to soft the tone of this conclusion. In the revised paper, we change "When the solar radiation is in a very low level in winter, it reaches the threshold level to prevent the OH chemical production, even by including the HONO production of OH." to "Because the solar radiation is in a very low level in winter, adding the photolysis of HONO has smaller effect in winter than in fall, and OH remains low values by including the HONO production term."

Specific comments:

(1) L167-169: there are no data to show the solar radiation are reduced We add a new figure and text to show the solar reduction.

(2) L185: same above Answered in the above.

(3) L188-190: same above Answered in the above.

(4) L199: "Chine" should be "China" Corrected.

(5) L201: removed "OH" Corrected.

(6) L218: what is "am" in O1D + am->O3P am represents air mass in chemical reaction equations.

(7) L222: "Madronich and Flocke (1999)" should be "(Madronich and Flocke, 1999)" Corrected.

(8) L295-296: one of "P1" should be "P2"? Corrected.

(9) L298-299: one of "P1" should be "P2" ? (10) L241: What are possible sources of HONO? Corrected. The possible sources of HONO could be surface sources or heterogeneous chemical reactions (but they are not fully understood at present).

Reference:

Zhang, L., Wang, T., Zhang, Q., Zheng, J., Xu, Z., & Lv, M. (2016). Potential sources of nitrous acid (HONO) and their impacts on ozone: A WRF/Chem study in a polluted subtropical region. Journal of Geophysical Research: Atmospheres, 121(7), 3645-3662.

Huang, R. J., L. Yang, JJ Cao, QY Wang, X. Tie, et al., Concentration and sources of atmospheric nitrous acid (HONO) at an urban site in Western China. Sci. of Total Environ., 593-594, 165-172, doi.org/10.1016/j.scitotenv.2017.02.166, 2017.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-354, 2019.

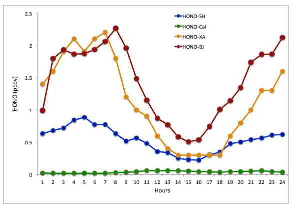

Fig. 6. The measured HONO concentrations (ppbv) in three large cities in China. The red line was measured in Xi'An from 24 July to August 6, 2015. The blue line was measured in Shanghai from 9 to 18 September, 2009. The dark-red line was measured in Beijing from 1 to 27 January, 2014. The green line is calculated by the WRF-Chem model. The measurement in fall of Shanghai is applied to the calculation for the OH production of HONO.

Fig. 1.

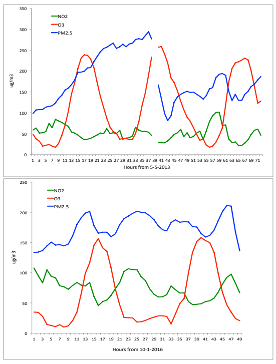

Fig.-A2. The diurnal variations of $PM_{2.5}$ (blue line) and O_3 (red line), and NO_2 (green line) during the periods (from May 5 to May 7, 2013 (upper panel) and from Oct. 1 to Oct. 2, 2016 (lower panel)).

Fig. 2.

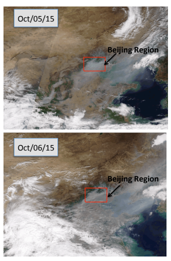

Fig-A3. The cloud condition during the period of the case study (between Oct 5 and 6, 2015 in the Beijing region. The bright white color shows the cloud covers, and the grey white shows the haze covers. The Beijing region is under the heavy haze conditions during the period.

Fig. 3.

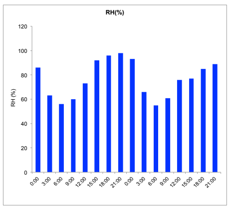

Fig-A4. The measured relative humidity (RH) conditions between Oct. 5 and Oct.6, 2015.

Fig. 4.

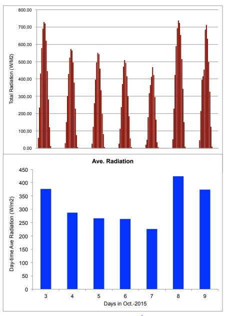

Fig-A5. The measured solar radiation (W/m^2) from Oct. 3 to Oct. 9, 2015 in Beijing. The upper panel shows hourly values, and the lower panel shows the daytime averaged values.

Fig. 5.