Author's response by Wenjie Wang et al.

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We greatly appreciate the time and efforts that the Referees spent in reviewing our manuscript. The comments are really thoughtful and helpful to improve the quality of our paper. We have addressed each comment below, with the Referee comment in black text, our response in blue text, and relevant manuscript changes noted in red text.

Referee #1

1. There is gap between ozone production and its concentration. A recent ACPD paper (Gao J.H. et al., doi:10.5194/acp-2020-140) and also references in the second paragraph of their Introduction Section highlighted that decreased ozone production by PM2.5 via affecting photolysis rates is much more than the reduction in surface ozone concentration. Moreover, a lot of different transport model studies (Xing J. et al., doi:10.5194/acp-17-9869-2017; Li J. et al. doi: 10.1016/j.scitotenv.2017.12.041; Li K. et al., doi:10.1038/s41561-019-0464-x) also show that the impact of PM2.5 on summer surface ozone is not important. I suggest, at least, the authors to do some detailed discussion to reconcile this important issue. This is particularly helpful for future studies.

Response: I agree with you that there is gap between ozone production and its concentration. I have given some detailed discussion to reconcile this important issue.

Line 542 - 558: Several three-dimension transport model studies show that the impact of $PM_{2.5}$ on summer surface ozone is not important (Li et al., 2018;Li et al., 2019b;Li et al., 2019a;Xing et al., 2017). Moreover, a recent study highlighted that decreased ozone production by $PM_{2.5}$ via affecting photolysis rates is much more than the reduction in surface ozone concentration (Gao et al., 2020). The difference between the two reductions in ozone production and surface ozone concentration indicates that, in addition to ozone photochemistry, there must be other ozone related physical processes influenced by the reduction in photolysis rate induced by aerosols. Model simulation indicates that aerosols lead to high concentrations of ozone aloft being

entrained by turbulence from the top of the planetary boundary layer (PBL) to the surface by altering photolysis rate and partly counteracting the reduction in surface ozone photochemical production induced by aerosols. In addition, the impact of aerosols on ozone from local and adjacent regions was more significant than that from long-distance regions (Gao et al., 2020). The accurate quantification of the effects of vertical mixing and long-distance transport on surface ozone concentration plays a critical role in the impact of aerosols on surface ozone, which needs further study in the future.

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2. Diurnal variation of ozone production. The authors take daytime average over 7:00-19:00 or (6:00-18:00?) for ozone production. I am not sure if the results may differ by narrowing the average to afternoon hours when ozone production is active and HOx levels are high. Also, Hollaway et al. (doi:10.5194/acp-19-9699-2019) show that PM2.5 impacts on the summertime photolysis of NO2 and ozone level at surface in Beijing are important before 11 am and after 3 pm but very limited in afternoon hours. I suggest the authors to show some diurnal information of simulated ozone production.

Response: I have analyzed the trend of simulated $P(O_3)$ in the afternoon hour (12:00-15:00), which increased at a rate of 1.3% yr^{-1}, lower than the increasing rate of daytime average $P(O_3)$. Diurnal variation of simulated $P(O_3)$ in 2013 is shown in Figure S1. The diurnal variation of simulated $P(O_3)$ in this study indicates that the influence of aerosols on $P(O_3)$ is still significant in the afternoon leading to $P(O_3)$ decreased by ~17%, which is slightly lower than the decrease in the whole daytime (25%) (Figure S2). This is because that the average AOD in the afternoon (1.4) is significantly higher than that before 11:00 am (0.94) and after 3:00 pm (1.1) despite lower SZA and lower light absorptive ability (i.e. higher SSA) in the afternoon.

Line 461-472: The simulated $P(O_3)$ in the afternoon hour (12:00-15:00) when ozone production is active and HOx levels are high increased at a rate of 1.3% yr^{-1}, which is lower than the increasing rate of daytime average $P(O_3)$ (2.2% yr^{-1}) (Figure S2). Hollaway et al. (2019) show that the impacts of aerosols on the summertime

photolysis of NO_2 and ozone at surface in Beijing are important before 11:00 am and after 3:00 pm but very limited in afternoon hours due to lower SZA and lower light absorptive ability of aerosol in the afternoon. However, the diurnal variation of simulated $P(O_3)$ in this study indicates that the influence of aerosols on $P(O_3)$ is still significant in the afternoon leading to $P(O_3)$ decreased by ~17%, which is slightly lower than the decrease in the whole daytime (25%) (Figure S3). This is because that the average AOD in the afternoon (1.4) is significantly higher than that before 11:00 am (0.94) and after 3:00 pm (1.1) despite lower SZA and lower light absorptive ability (i.e. higher SSA) in the afternoon.

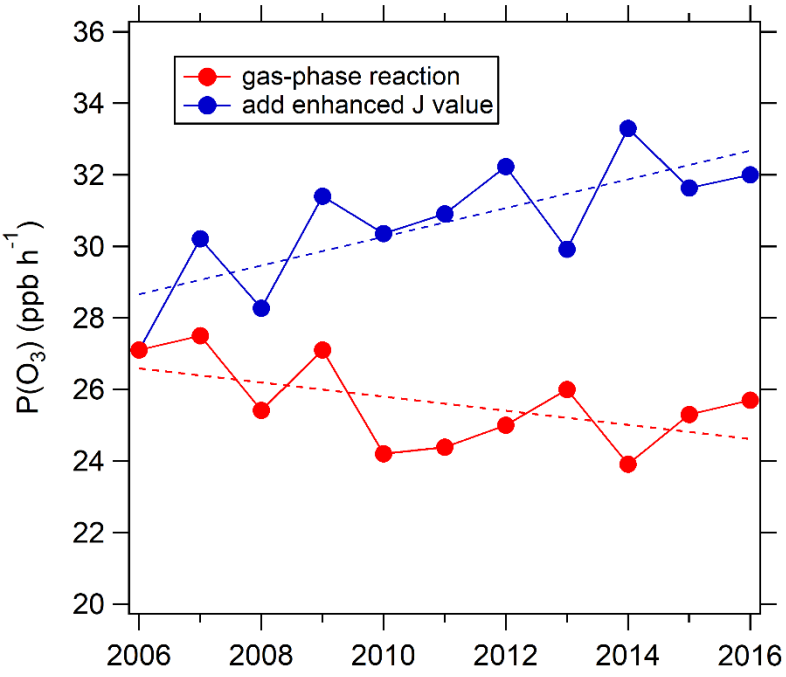

Figure S2. Trend of monthly afternoon (12:00-15:00) mean $P(O_3)$ simulated by the chemical box model. Red dots: Only the gas-phase reactions are considered in the box model constrained by observed photolysis frequencies from 2006 for all eleven years. Blue dots: the box model as above, but constrained by the photolysis frequencies derived for each year.

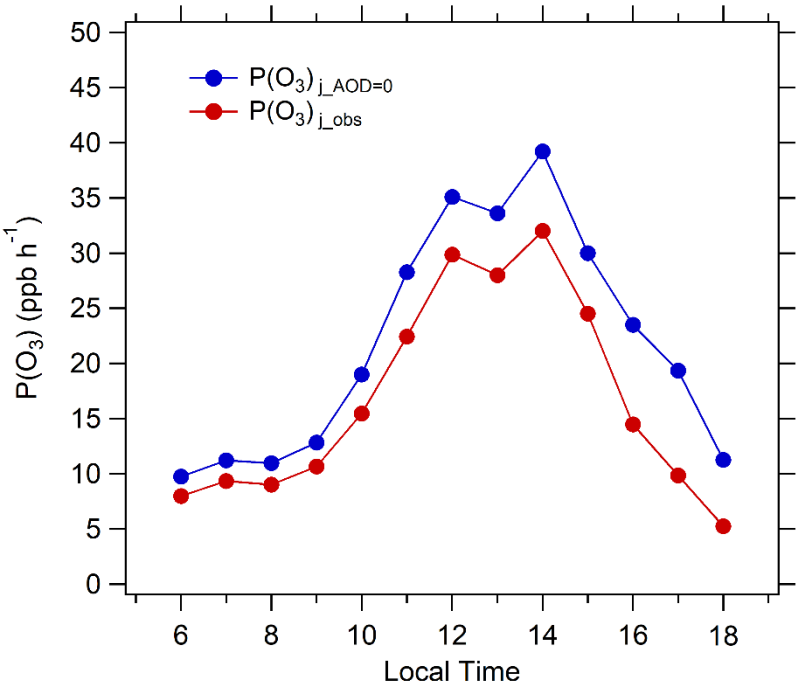

Figure S3. Diurnal variation of simulated $P(O_3)$ in Beijing in August during 2005-2016. $P(O_3)_{j\_obs}$ represents ozone production rate under observed photolysis frequencies; $P(O_3)_{j\_AOD=0}$ represents ozone production rate under calculated photolysis frequencies when AOD is equal to 0.

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3. The authors show an important result of an increased SSA in Beijing (Fig.12). More importantly, there is a shift pattern of j(NO_2) over 2006-2016 that the crossing point between J(NO2) profile of 2006 and zero AOD profile changed from above PBL to below PBL in 2016. I think this means that the role of PM2.5 may be more important under condition like 2006, but will be limited under condition like 2016 when there is offsetting effect for PBL ozone by vertical mixing. This may deserve a discussion.

Response: Yes, I agree with you. This is a good point. I have given a brief discussion according to your suggestion.

Line 533-541: However, there is a shift in the vertical profile of j(NO_2) that is important. The crossing point between j(NO_2) profile of 2006 and zero AOD profile is below PBL, while in 2016 the j(NO_2) profile crosses the zero AOD profile within the PBL. This means that as the AOD is reduced further, changes in the vertical average

j(NO_2) will be limited, since increases in j(NO_2) near the top of the PBL will compensate for decreases near the surface. Additionally, this also denotes that the role of $PM_{2.5}$ may be more important under condition like 2006, but will be limited under condition like 2016 when there is offsetting effect for PBL ozone by vertical mixing caused by larger ozone vertical gradient (Gao et al., 2020).

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4. Some other specific comments. (1) It is confused to see 2005-2016 and 2006-2016 in the text. Please clarify this. (2) I suggest to use p-value other than the r square where there is a trend analysis. (3) Line 290: Shanghai should be "the south to North China Plain". (4) Lines 293-296: how about the role of regional contribution outside of Beijing? For example, the increasing emissions in the whole North China Plain. (5) Line 494: Please take caution when saying "ozone increase". you mean surface ozone concentrations?

Response: (1) NOx data in 2005 were not available. Therefore, the trend of NOx during 2006-2016 was analyzed. In addition, we focus on the trend of P(O_3) during the period of 2006-2016 due to the lack of NOx data in 2005. (2) Thank you. I have summarized p-values for the temporal trend of all parameters in table 2. (3) Thank you. I have revised it. (4) In this study, we mainly focus on the variation of the local ozone production. It is difficult to give an accurate estimation of the regional contribution outside of Beijing. Previous studies have reported that regional transport from neighboring provinces outside Beijing (including Hebei, Tianjin and Shandong) contributed about 35%-60% of ozone in Beijing during high ozone episodes (Streets et al., 2007;Wang et al., 2020). I have analyzed the ozone trend in Changdao site, a background site in the east of North China Plain, to discuss the regional contribution outside of Beijing due to increasing emissions in the whole North China Plain. This site is nearly not influenced by local anthropogenic emissions. MDA8 ozone concentrations at the Changdao site increased slowly (+1.2 ppbv yr^{-1}, r^2 = 011, p=0.25) during 2013-2019, which is about a half of the increasing rate of MDA8 ozone concentrations at PKUER site (+2.3 ± 1.2 ppbv yr^{-1}, r^2=0.66) during 2006-2016.

345-346: NOx data in 2005 were not available. Therefore, the trend of NOx during 2006-2016 was analyzed.

438-439: We focus on the period during 2006-2016 due to the lack of NOx data in 2005.

Line 657-658:

Table 2. p value of temporal trends for different parameters.

Parameter	Period	r^2	p value	P value <0.01?	P value <0.05?
median	2005-2016	0.63	0.002	yes	yes
perc98	2005-2016	0.11	0.288	no	no
DTAvg	2005-2016	0.47	0.014	no	yes
MDA1	2005-2016	0.32	0.057	no	no
MDA8	2005-2016	0.66	0.001	yes	yes
4MDA8	2005-2016	0.42	0.023	no	yes
AOT40	2005-2016	0.67	0.001	yes	yes
NDGT70	2005-2016	0.56	0.005	yes	yes
SOMO35	2005-2016	0.57	0.004	yes	yes
exceedance	2005-2016	0.32	0.054	no	no
Ox	2005-2016	0.38	0.044	no	yes
CO	2005-2016	0.87	0.001	yes	yes
VOC reactivity	2005-2016	0.52	0.006	yes	yes
NO_X	2006-2016	0.81	0.001	yes	yes
Calculated $j(NO_2)$	2006-2016	0.94	0.000	yes	yes
AOD (380 nm)	2006-2016	0.78	0.000	yes	yes
$PM_{2.5}$	2009-2016	0.93	0.000	yes	yes
Sa	2006-2016	0.51	0.010	yes	yes
SSA	2005-2016	0.70	0.001	yes	yes
AE	2005-2016	0.03	0.593	no	no
COT	2005-2016	0.003	0.875	no	no
Total O_3 column	2005-2016	0.15	0.215	no	no

Line 307-309: Additionally, there were very small trends of O_3 concentrations at the background site (Dongtan) in Shanghai, located to the south of the North China Plain (Gao et al., 2017).

Line 309-317: However, these background sites in Beijing and Shanghai may be strongly affected by local emissions. MDA8 ozone concentrations at the Changdao site, a background site in the east of the North China Plain that is much less

influenced by local emissions, increased slowly (+1.2 ppbv yr^{-1}, r^2=0.11), but that rate is not statistically significant (p = 0.25) during 2013-2019 (Figure S1). Based on these reports of smaller and variable trends, we assume that the trend in regional background ozone in the North China Plain made only a minor contribution to the relatively larger ozone trend observed at the PKUERS site (+2.3 ± 1.2 ppbv yr^{-1}, r^2=0.66, p = 0.001).

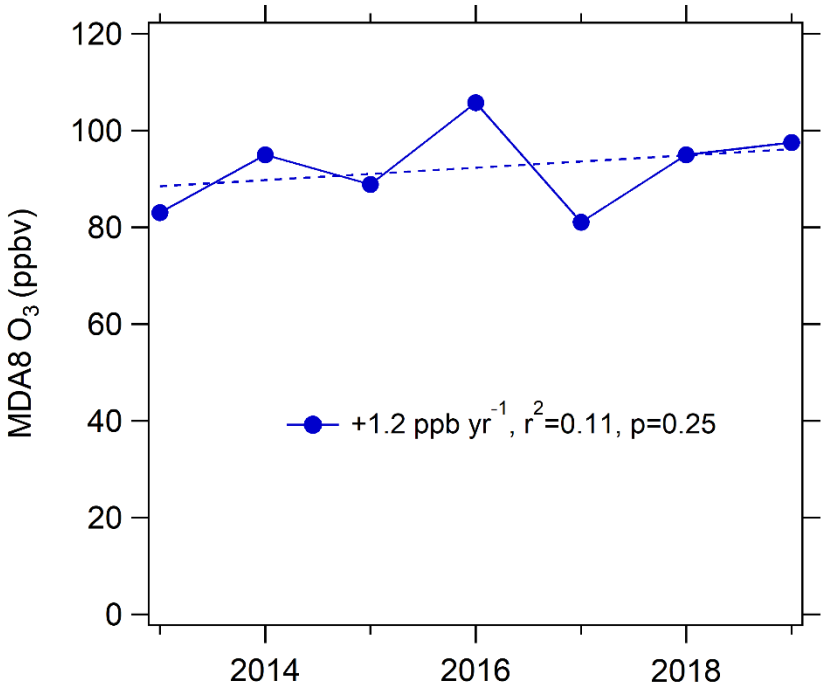

Figure S1. The trend of average MDA8 ozone in Changdao during 2013-2019. These data is acquired from "Blue book on prevention and control of atmospheric ozone pollution in China (in Chinese)" reported by Chinese Society of Environmental Sciences in 2020 (http://www.epserve.com/forepart/zxnr_index.do?oid=51478637&tid=26378242).

Referee #2

1. Regional transport is also a key source of surface ozone. This work tried to assess the impact of regional O3 by analyzing measurements at a regional background site. This is not sufficient because this site was largely affected by Beijing emissions. I suggested that other background sites can be employed or backtransjectories at typical year can be used to analyze the impact of regional transport.

Response: I agree with you that the regional background site in Beijing was largely affected by Beijing emissions. I have chosen another site in Changdao, Shandong province, which is nearly not influenced by local emissions and thus is a better background site in North China Plain. MDA8 ozone concentration at the Changdao site increased at a rate of 1.2 ppbv yr^{-1} (r^2=0.11) during 2013-2019, which is significantly smaller than that at PKUER site during 2006-2016 (2.3 ppbv yr^{-1}, r^2=0.66) and during 2013-2019 (2.0 ppbv yr^{-1}, r^2=0.67).

Line 309-317: However, these background sites in Beijing and Shanghai may be strongly affected by local emissions. MDA8 ozone concentrations at the Changdao site, a background site in the east of the North China Plain that is much less influenced by local emissions, increased slowly (+1.2 ppbv yr^{-1}, r^2=0.11), but that rate is not statistically significant (p = 0.25) during 2013-2019 (Figure S1). Based on these reports of smaller and variable trends, we assume that the trend in regional background ozone in the North China Plain made only a minor contribution to the relatively larger ozone trend observed at the PKUERS site (+2.3 ± 1.2 ppbv yr^{-1}, r^2=0.66, p = 0.001).

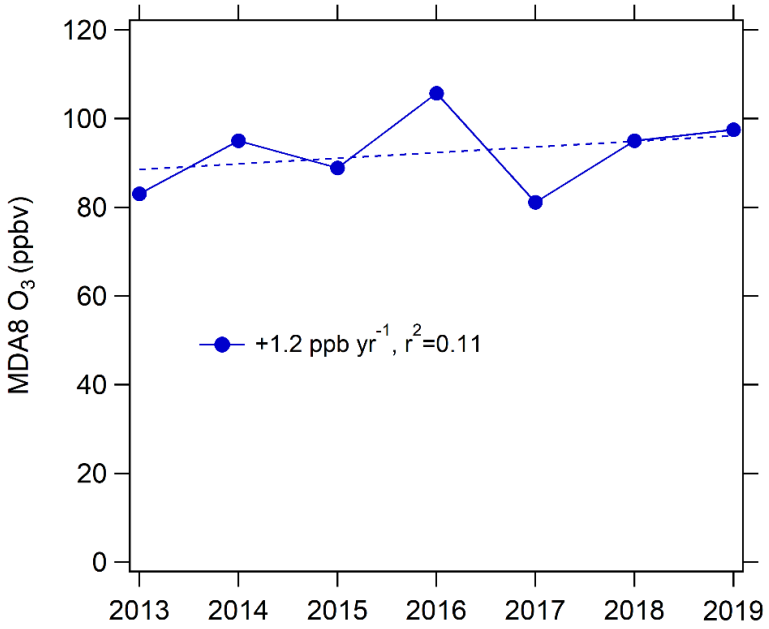

Figure S1. The trend of average MDA8 ozone in Changdao during 2013-2019. These data is from "Blue book on prevention and control of atmospheric ozone pollution in China (in Chinese)" reported by Chinese Society of Environmental Sciences in 2020 (http://www.epserve.com/forepart/zxnr_index.do?oid=51478637&tid=26378242).

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2. Recent, a few heteorogeneous chemical reactions are thought to be potential factors of ozone. For example, photolysis of HNO3 ($NO3^-$) adsorbed on the solid surface of aerosol particles effectively produces HONO and NOx in the gas phase (Salgado and Rossi et al., PCCP,2002; Ramazan, 2006). A short disscuss should be performed.

Response: Thank you! I agree with you that A few heterogeneous chemical reactions of nitrogen oxides are thought to be potential influential factors of ozone production. I have added heterogeneous uptake of N_2O_5, NO_2 and NO_3 in the chemical box model to test its effect on ozone production. Our simulation indicates that the reduced heterogeneous uptake of NOx caused $P(O_3)$ to increase by only ~2.5 % during 2006-2016.

Line 249-253: Heterogeneous uptake of N_2O_5, NO_2 and NO_3 was included in the chemical box model. This includes $\gamma_{N2O5} = 0.007$ for converting N_2O_5 to HNO_3 (Wang et al., 2017), $\gamma_{NO2} = 1 \times 10^{-5}$ for conversion of NO_2 to HONO and HNO_3 (which yields a good simulation of $HONO/NO_2$ concentration ratios in China (Shah et al., 2020)) and $\gamma_{NO3} = 1 \times 10^{-3}$ for conversion of NO_3 to HNO_3 (Jacob, 2000).

Line 487-495: A few heterogeneous chemical reactions of nitrogen oxides are thought to be potential influential factors of ozone production. For example, the heterogeneous uptake of NO_2 to produce HNO3 and HONO, and the heterogeneous uptake of NO_3 and N_2O_5 to produce HNO_3. Our simulation indicates that the reduced heterogeneous uptake of NOx caused $P(O_3)$ to increase by only ~2.5 % during 2006-2016. K Li et al. [2019a] reported that the effect of heterogeneous uptake of nitrogen oxides on ozone is very small under VOC-limited and summertime conditions in North China Plain. Our simulated result in Beijing where is under VOC-limited and summertime conditions is consistent with the result of Li et al. [2019a].

Reference:

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