Dear Editors:

We are submitting the revised manuscript acp-2020-385 together with point-by-point responses to the reviewer' comments. We appreciate the reviewers for the valuable comments. We hope you and the reviewers are satisfied with our responses and revision.

The major changes made in the revised version include:

1. Added hourly in-situ NO_2 measurement analyses in the supplement.
2. Added additional discussions about the tropospheric O_3 transport and synoptic pattern effects on surface O_3 in the revised manuscript.
3. Added explanations about the preponderant role of NO titration in surface ozone increase in the revised manuscript.
4. Added the average diurnal profiles of pollutants in the revised supplement.
5. Increased a detailed model description in the manuscript.
6. Replotted Fig. 7b to ensure a better readability.
7. Added discussion about radiation uncertainties to aerosols (AOD and SSA) about Fig. 6b.
8. Added more discussions on the role of the boundary layer and changing meteorology in O_3 trends.
9. Added a discussion on the HOx chemical source in the revised manuscript.

We look forward to hearing from you regarding our revision soon.

On behalf of the co-authors,

First Author: Xiaodan Ma
Corresponding Author: Jianping Huang

Point-by-point responses to the Comments/Suggestions of Reviewer #1

Overview

The paper deals with the rapid increase in summer surface ozone over the North China Plain during 2013–2019 and the hypothesis that this decrease would be a side effect of reduction control of atmospheric particulate matter is examined. I would suggest publication of the paper, after the issues raised below are addressed.

General comments

1. I think that there are some key measurements missing in order to undertake a proper review of this manuscript. The most important is the lack of hourly in-situ NO_2 measurements from the same stations providing the hourly ozone measurements, so that to be able to check if the ozone increase is directly related to the corresponding NO_2 decrease of surface concentrations The reason is that it is already known that for most urban stations the sum $NO_2+O_3=O_X$, called also potential ozone is constant (e.g. Kley et al., 1994; Kalabokas et al., 2000), so that any NO_2 decrease is directly related with an exactly equivalent increase in ozone (in ppb) through reaction with ozone (NO titration), which is very rapid. The presented data of total NO_2 column might provide some indication on that, but it is expected to be less efficient than in-situ measurements.

Thank the reviewer for the suggestion. The in-situ NO_2 measurements are now included in supplementary material for a comparison between year 2013 and year 2019 (See Fig.S4 in the supplementary material and Fig.T1 attached with this letter). The in-situ measured NO_2 showed a similar decreasing trend to the total column NO_2 (see Fig.S5 in the supplementary material and Fig. T2 with this letter).

To better understand the relationship of increase in surface O_3 with the decrease in NO_2, the change in monthly mean Ox (a sum of O_3 and NO_2) is plotted in Fig. T3 (see Fig.S2 in the supplementary material). It is clear that Ox showed an increasing trend over the past 7 years during daytime and nighttime in both Beijing and the NCP region. The decrease in NO_x emissions could be part of the main reasons causing the rapid increase in O_3 over the NCP region where O_3 formation is dominated by the VOC-limited regime, but we do not see that "any NO_2 decrease is directly related with an exactly equivalent increase in ozone (in ppb) through reaction with ozone (NO titration)" as the reviewer expected. In fact, this is consistent with the statement that Ox is a conservative quantity (Kley et al., 1994) since we are looking at the changes over a long-time period (i.e., 7 years) rather than a short time period.

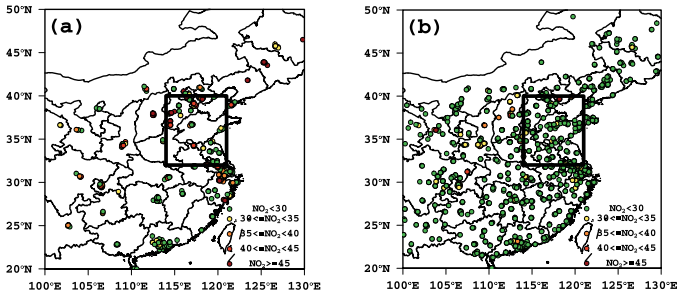


Figure T1. A comparison of spatial distributions of monthly mean of NO_2 (μg m^{-3}) monitored by China National Environmental Monitoring Center between (a) 2013 and (b) 2019 in eastern China (NCP indicated by the box).

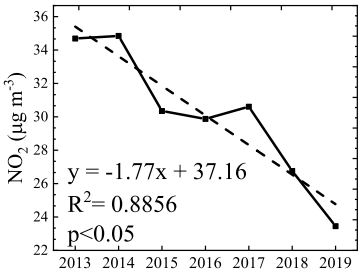


Figure T2. Long-term changes in monthly mean of observed NO_2 averaged over the North China Plain in June over the period of 2013–2019.

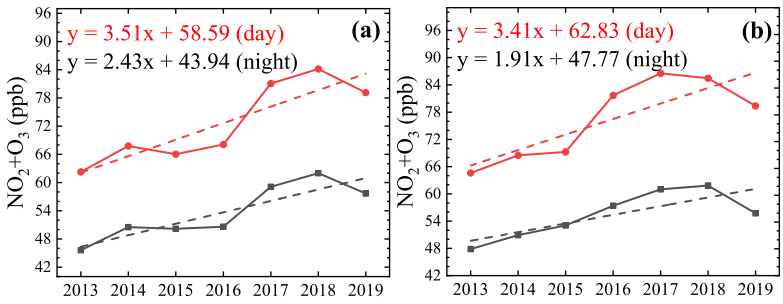


Figure T3. Long-term changes in monthly mean of observed Ox (NO_2 +O_3) averaged over the North China Plain (a) and urban areas Beijing in daytime (redline) and nighttime (blackline) in June over the period of 2013–2019.

2. In addition, the issue of tropospheric ozone and its subsequent influence to the boundary layer and surface background ozone concentrations should be also taken into account. In

relation to that, in my opinion, a weak point of the paper is that the levels of measured surface ozone are mainly related to the photochemical ozone production over the examined region of China. On the other hand, the issue of background ozone levels and their variability within the boundary layer and the free troposphere are not (or very little) discussed. For this purpose, I think that it would be quite helpful to take into account a relatively recent extended review paper on tropospheric ozone on global scale, including SE Asia which is one of the most important global tropospheric ozone hotspots (Gaudel et al, 2018, Elem Sci Anth, 6: 39. DOI: https://doi.org/10.1525/elementa.291 and also references therein). From my perspective and based on my expertise of analyzing ozone episodes in the Mediterranean region, I would just point out that the possibility of vertical ozone transport in the troposphere influencing the boundary layer and surface ozone values (a major factor in the Mediterranean, especially in its eastern part during summer but also in its western part during spring) is not mentioned in the manuscript and so all measured ozone is considered to be produced by local photochemistry from precursor pollutant emissions emitted in China only. This might not be always the case, especially during the May-September period when the tropospheric influence to the boundary layer gets its maximum height while at the same time the tropospheric ozone maxima are observed during the same period of the year, with subsequent influence to the boundary layer and surface ozone values depending on the prevailing synoptic meteorological conditions.

We agree with the reviewer that the change in tropospheric O_3 could exert an important impact on ozone in the atmospheric boundary layer (ABL) or near surface. For instance, Jiang et al. (2015) presents an ozone episode in the southeast costal of China, and found that the downward transport of O_3 from the UTLS region driven by a typhoon is the key factor causing a large increase in surface O_3 by 21-42 ppb. In addition, East Asia including the NCP region is considered as a net export region of O_3 from the ABL rather than an import (e.g., Cooper et al., 2010; Lin et al., 2012a). The long-range transport of O_3 from Africa may exert an important impact on O_3 peaks in Asia around 25^0N, i.e., the south of our study area, NCP (32^0N-40^0N) with the largest impact in boreal winter and early spring (>10 ppb) and the lowest in boreal summer (<6ppb) (Han et al., 2018; Gaudel et al, 2018).

The impacts of downward transport of tropospheric O_3 and regional transport are not included in our current study mainly due to two reasons. First, the MM model does not have a capability of simulating vertical transport. Second, no vertical observational data (like ozone sounding or Lidar observational data in this region over the study period) are available.

However, according to the reviewer's suggestion, we have added additional discussions on background ozone levels and their variability within the boundary layer and the free troposphere and their impact on the increase in surface O_3. The seasonal distributions of O_3 in the upper troposphere (UT) show a summer maximum that coincides with the maximum photochemical activity in the North Hemisphere (Gaudel et al, 2018). A broad spring/summer ozone enhancement across northern mid-latitudes with a band of enhanced summertime ozone stretching from North Africa, across the Mediterranean Sea to East Asia at 5–7 km and 7–9 km has been detected (Worden et al., 2009). Under favorable synoptic patterns, the high O_3 in the UT may exert an important impact on surface O_3 concentrations (e.g., Kalabokas et al., 2013;

Kalabokas et al., 2017).

Added discussion can be found in L433-443 of the revised manuscript.

In relation to the above, tropospheric vertical ozone measurements over China (e.g. Ding et al., 2008; Zhang et al., 2020) would be needed for a thorough assessment together with tropospheric satellite ozone data. In addition, synoptic weather patterns might influence greatly the tropospheric as well as the surface ozone concentrations (e.g. Kalabokas et al., 2013; Kalabokas et al., 2017) and this issue is not discussed.

Assessment of the change in tropospheric O_3 is an attractive topic, and we like to pursue it in another study separately. To our knowledge, tropospheric O_3 retrieved from satellite measurements remains a large uncertainty given 90% of total O_3 is located in the stratosphere. In addition, no ozone sounding data (e.g., Zhang et al., 2020) and other observations such as Measurement of Ozone by Airbus In-service airCraft' (MOZAIC) program data (Ding et al., 2008) are available for performing further analysis in this region during the study period. We admit that the MM model used in this study does not have a capability of quantifying the impact of vertical transport on surface O_3, and we have included this issue in our discussion. "The impact of tropospheric O_3 should be taken into account when the observational data available in NCP region." (see L441-443).

We agree with the reviewer that synoptic pattern may exert an important impact on tropospheric and surface O_3 concentrations. For instance, high concentrations of surface O_3 or O_3 episodes occurred in western Mediterranean and central Europe were usually linked with anticyclone synoptic pattern which led to a large-scale subsidence, clear sky, and high temperature (e.g., Kalabokas et al., 2013; Kalabokas et al., 2017). Yin et al. (2019) concluded that synoptic patterns played a critical role in summer ozone pollution in eastern China. Under the control of zonally enhanced East Asian deep trough, the local hot, dry air and intense solar radiation enhanced the photochemical reactions and produced more O_3. The inter-annual magnitude variations of the domain synoptic patterns may have an important impact on surface O_3 episodes, and its impact on the long-term changes needs a further investigation. Thus, we include discussion on impact of individual meteorological factors such as air temperature, the atmospheric boundary layer height, etc. rather than synoptic patten on long-term surface O_3 in our study.

To address reviewer's comment, we added our discussions on this comment in the revised version (see L444-452 in the revised version).

Overall, I think that the submitted paper presents some interesting data and ideas regarding the recent increasing trend of surface ozone in China but I think that the above described missing information is essential for a proper review of this manuscript.

Thanks for positive comments and we tried our best to include all the available observational data in this study. In-site NO_2 measurements are included in the revised version as suggested.

Specific comments

Page 2, lines 216-220: This is reasonable as higher NO/NO2 levels increase the ozone destruction in urban and semi urban stations, through NO titration.

Thanks for comments. We agree that higher NO/NO_2 levels contribute to more ozone through NO titration.

Page 9, lines 235-236: This applies to stations with low NO emissions in their surroundings. As mentioned before in most urban and semi urban stations, the NO titration is the controlling factor.

Thanks for comments. We have added the discussion on NO titration in the manuscript.

Page 14, lines 379-386: This in fact reflects the preponderant role of NO titration. Lower NO emissions destroy less ozone, which in most stations is originated from the tropospheric/boundary layer background.

Thanks for your comments. We added additional explanation on the preponderant role of NO titration in surface ozone increase in the revised manuscript (see L402-403).

Supplement: I would suggest plotting also the average diurnal profiles of pollutants (O3, PM2.5) per season, at least for spring and summer.

Thanks for suggestion. We added the average diurnal profiles of pollutants in the revised supplement (See Fig.S6 in the supplementary material).

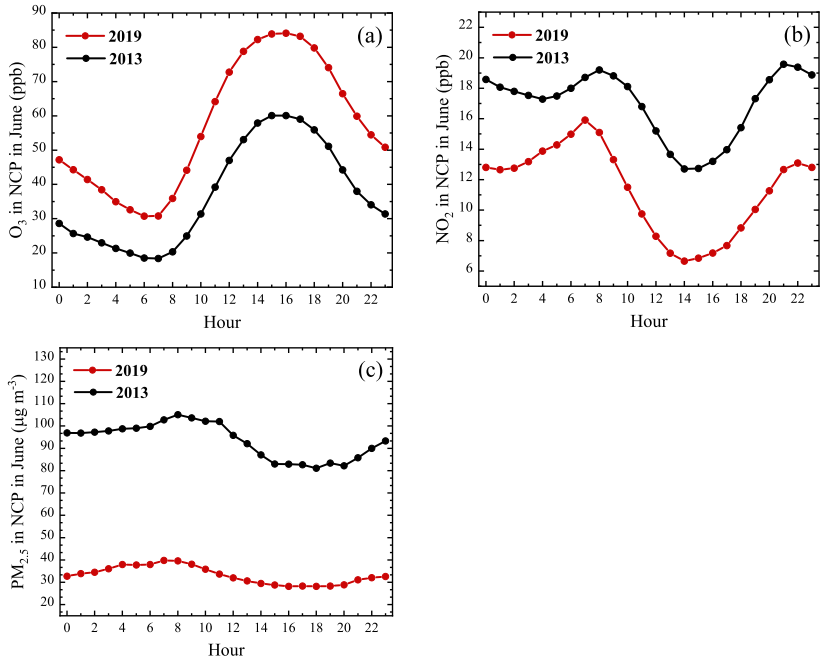


Figure T4. Average diurnal profiles of (a) O_3, (b) NO_2, (c) $PM_{2.5}$ in June of 2013 (black lines) and 2019 (red lines).

Technical comments

Page 26, line 665 (Fig. 3): PBLH (g, h).

Thanks. It's revised.

Point-by-point responses to the Comments/Suggestions of Reviewer #2

This manuscript uses observations (including in situ and remote sensing data) and box model simulations to examine the trend of O_3 over North China Plains during 2013-2019 and its impacting factors including emissions, AOD, SSA, temperature and boundary layer height (PBLH). The contribution to O_3 formation from each impacting factor is quantified and found that reduction of emissions and aerosol radiative effects are the dominant factors that contribute to O_3 increase from 2013 to 2019. Such analysis help understand O_3 chemistry over NCP and help develop effective control strategies on reduction of ambient O_3. The manuscript is written well and clearly. This reviewer would recommend publication after addressing the following comments.

Specific comments:

1. The assumptions made in box model simulations need to be described more clearly. According to LN161, "This model computes time-dependent chemical evolution of an air parcel initialized with a known composition, assuming no additional emissions, no dilution and no heterogeneous processes", the model only takes initial concentration of chemical species, radiation and temperature and compute evolution of concentrations. It cannot directly quantify "the relative contributions of anthropogenic emissions and aerosol optical and radiative properties to the change in surface O_3" stated on LN151. A few assumptions must have been made. How does the model account for different NOx and VOCs emissions, and PBLH?

Thanks for pointing out the problem. Indeed, something was mixed up in the original description. NOx and VOCs emissions were changed to assess the impact of emissions on surface O_3 simulations (see Table 1). Dry deposition is included in all the simulations and sensitivity runs. The PBLH was ingested as the model requests every 4 hours to support the calculation of entrainment term.

The issue is corrected and can be found in the revised version. “This model computes time-dependent chemical evolution of an air parcel initialized with a known composition and additional emissions. It is assumed that no dilution is included in the simulations given the difficulty of getting inputs to calculate the dilution rate. The transport in and out of air pollutants reached a quasi-equilibrium state over the study domain and no heterogeneous processes was included in the MM model.” (see L161-165).

LN187, using meteorological data at a 4-hour interval appears too coarse/crude to reproduce diurnal variation of O_3. Why not use hourly values?

Yes, theoretically, hourly input data could reproduce more reasonable diurnal variations in surface O_3 simulations. However, according to our tests, the computational time increased substantially when input data were ingested hourly. Meanwhile, the MM model was able to capture the diurnal variation pattern reasonably when the input data were ingested every 4 hours. Thus, we decided to ingest the input data every 4 hours for all the numerical simulations and

sensitivity studies.

2. The diurnal variation of O_3 depends on the nighttime O_3 depletion due to NO titration and dry deposition and daytime O_3 formation after rush hour emissions. The box model does not account for dry deposition and additional rush hour emissions. It is a little surprising the box model can still capture the full diurnal variation of O_3 in Fig. 7.

Sorry for the confused. Dry deposition, time-varying meteorological inputs and emission drivers were included in the MM model. With such settings, the MM model was able to capture the diurnal variation in surface O_3. Such an information is included in the revised version (see L160-165 and L183-193).

3. What is the purpose of sensitivity of jNO_2 to different solar zenith angle in Figs. 8 and 9? which should not vary from 2013 to 2019. In another word, solar zenith angle is not a factor for O_3 variation from 2013-2019.

The solar zenith angle is not a factor in driving the increase in surface O_3 from 2013 to 2019. The main purpose of Figures 8 and 9 is to examine the sensitivity of jNO_2, the daily 8-hr maximum O_3 and HO_2 radicals to the changes in AOD and SSA. The solar zenith angle is included in the figures for a comparison since both jNO_2 and HO_2 radicals are very sensitive to changes in solar zenith angle but show very different change trend with varying solar zenith angle. For instance, jNO_2 shows a nearly linear change with Sec (θ) wheras HO_2 doesn't. On the other hand, jNO_2 shows the largest sensitivity to AOD and SSA at noontime while HO_2 has a largest sensitivity around 3:00 pm local standard time which is consistent with the peak hour of surface O_3.

LN59, $TCNO_2$ was reported to be increased by 307% in Beijing from 1996-2011, but it decreased from 2013-2019 in Fig. 2. Are they consistent?

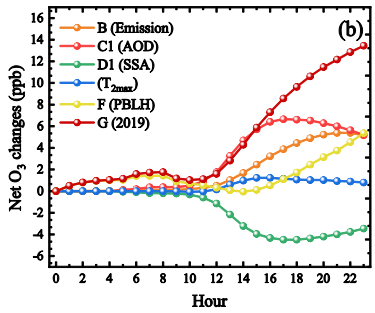
Yes, they are correct. 2013 was the transition year. The change trend was reversed around 2013 since a strict NOx emissions control measures were implemented in China (e.g., Huang et al., 2013; Zeng et al., 2019).

LN115 what is "ppb a-1"? ppb/year?

Yes. "ppb a-1" represent ppb per annual (year). Corrected.

Fig. 7b needs to be improved, different lines are hard to read.

Thanks for the suggestion, the figure is replotted with better color identification to improve readability.



LN97, " reducing heterogeneous uptake of reactive gases (mainly HO_2 and O_3), of which the latter is more important". Box model appears more suitable to investigate such an impact.

Yes, the current box model needs to include a detailed aerosol chemistry and observation-based uptake coefficients to achieve the target. We added this in the revised version (see L412-413).

Fig. 5g may be misleading. The positive correlation between PBLH and O_3 may be simply because on those high PBLH cases, radiation and temperature are much higher, thus O_3 formation is stronger. Many papers report that shallower PBL suppresses dispersion of pollutants and leads to higher O_3, suggesting a negative correlation between PBLH and O_3.

We agree. This could represent one of the cases when radiation is strong, temperature is higher while the PBL height is higher either. Higher height of the PBL also could lead to the mixing of near surface air with the O_3 rich air aloft, resulting in the observed enhancements in surface O_3 (Reddy et al., 2012). O_3 formation could be suppressed by the a shallow PBL due to the NO titration. We have added an additional statement "On the other hand, some studies found a negative correlation between the PBLH and O_3. They claimed that a shallower PBL may suppress the dispersion of pollutants and lead to higher O_3 (Yan et al., 2018; Jiang et al., 2016; Wei et al., 2016; Huang et al., 2005)". Please see the revised version (in L304-310).

Sensitivity simulations summarized in Table 1 appears to attribute radiation uncertainties to aerosols (AOD and SSA). Cloud may also play critical roles, which might be the reason to explain the poor correlation between radiation and aerosol concentrations in Fig. 6b.

Thanks for the comment. We have added the statement with "cloud may also play a critical role, which might be another reason to explain the poor correlation between radiation and aerosol concentrations in Fig. 6b" in the revised version.

Point-by-point responses to the Comments/Suggestions of Reviewer #3

Overview

The paper in its present form is clearly written and could be published after revisions. At this stage of the review process, I would like to add a few points and suggestions to be carefully addressed by the authors:

General comments

1. Since the focus of the paper is on the response of ozone to possible forcing processes, I wonder why so little is said about the role of heterogeneous chemistry. There is growing evidence that the increase in ozone is related to the increase in HO_2 due to the reduced scavenging of HO_2 by aerosols (PM) more than a change in the J-values. The paper highlights the change in the $J(NO_2)$ due reduced PM concentrations, but does not provide the quantitative response associated with the change in heterogenous processes. It would be important to discuss this aspect, even if no specific simulation of this effect has been done.

Thanks for the reviewer's suggestion. According to recent researches, decrease in $PM_{2.5}$ was considered as one of the important causes leading to such an increase in surface O_3 mainly due to additional O_3 production associated with reduced sink of hydroperoxyl radicals (HO_2) (Li et al., 2019a). They pointed out that increase in surface O_3 associated with decrease in $PM_{2.5}$ was more prominent than that with reduction of NOx emissions over the NCP region where O_3 formation was dominated by VOC-limited regime. Liu and Wang (2020a, 2020b) found the reduction of PM emissions increased the O_3 levels by enhancing the photolysis rates and reducing heterogeneous uptake of reactive gases (mainly HO_2 and O_3), of which the latter is more important than the former. However, the MM model does not include aqueous-phase chemistry that has been implemented in the 3D meteorology/chemistry models (e.g., Li et al., 2019a; Liu and Wang, 2020a, 2020b). Thus, inclusion of detailed aerosol chemistry and observation-based uptake coefficients in a box model like MM is necessary to provide more accurate assessment of impact of aerosol radiative effect on surface O_3 change in the future.

We have included the related discussion about the role of heterogeneous chemistry both in the Introduction and Discussion part (See L92-98 and L407-413).

2. A more convincing discussion must be provided regarding the role of the boundary layer, the changing meteorology (e.g., average cloudiness, precipitation, etc.,) and the surface deposition processes. Some of these may not be explicitly treated in a box model, but should be discussed with appropriate references.

Thanks for the comment. We agree with the reviewer that the boundary layer and the changes in other meteorological factors such as cloudiness, precipitation etc. played an important role in increase in surface O_3. In fact, we have conducted two cases (cases F and G in Table 1) to assess the impact of the planetary boundary layer height (PBLH) on the change in surface O_3. In addition, we have included two cases (i.e., E and G in Table 1) to investigate the impact of surface maximum air temperature on increase in surface O_3. To highlight the reviewer's concern with the role of changing meteorology, we cited a relevant reference on this topic, "The

influence of changing meteorological factors on the change trend in surface O_3 may vary greatly with regions and time. In addition to air temperature and the boundary layer conditions, other meteorological factors such as cloud cover, precipitation, wind fields played an important role in driving the changes in surface O_3 observed in many places of China (e.g., Liu and Wang, 2020a)" (see L416-420).

3. There should be a discussion about the processes that have changed HO_x chemistry (which affects the ozone production and loss) and this includes, for example, the HONO and formaldehyde photolysis.

We agree with the reviewer that HO_x chemistry is an important factor affecting the production and loss of O_3. Now a statement with "The HONO photolysis as the primary production of OH radicals and the formaldehyde (HCHO) photolysis as the net radical source of HO_2 can lead to major changes in the HOx and NOx budget that may have an important effect on O_3 production and loss (e.g., Aumont et al., 2003; Brasseur et al., 2006; Lin et al., 2012b)" is added on the revised version (see L174-179).

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Rapid increase in summer surface ozone over the North China Plain during 2013–2019: a side effect of particulate matters reduction control?

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Abstract. While the elevated ambient levels of particulate matters with aerodynamic diameter of 2.5 micrometers or less ($PM_{2.5}$) are alleviated largely with the implementation of effective emission control measures, an opposite trend with a rapid increase is seen in surface ozone (O_3) in the North China Plain (NCP) region over the past several years. It is critical to determine the real culprit causing such a large increase in surface O_3. In this study, seven-year surface observations and satellite retrieval data are analyzed to determine the long-term change in surface O_3 as well as driving factors. Results indicate that anthropogenic emission control strategies and changes in aerosol concentrations as well as aerosol optical properties such as single-scattering albedo (SSA) are the most important factors driving such a large increase in surface O_3. Numerical simulations with National Center for Atmospheric Research (NCAR) Master Mechanism (MM) model suggest that reduction of O_3 precursor emissions and aerosol radiative effect accounted for 45 % and 23 % of the total change in surface O_3 in summertime during 2013–2019, respectively. Planetary boundary layer (PBL) height with an increase of 0.21 km and surface air

temperature with an increase of 2.1 °C contributed 18 % and 12 % to the total change in surface O_3, respectively. The combined effect of these factor was responsible for the rest change. Decrease in SSA or strengthened absorption property of aerosols may offset the impact of AOD reduction on surface O_3 substantially. While the MM model enables quantification of individual factor's percentage contributions, it requires further refinement with aerosol chemistry included in the future investigation. The study indicates an important role of aerosol radiative effect in development of more effective emission control strategies on reduction of ambient levels of O_3 as well as alleviation of national air quality standard exceedance events.

1 Introduction

Elevated ambient levels of ozone (O_3) are of great concern due to their important impact on human health, ecosystem productivity, atmospheric chemistry, and climate change (Monks et al., 2015; Tai et al., 2014; Tan et al., 2019). O_3 is produced by a series of photochemical reactions involving nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs) in the presence of solar radiation. Ambient levels of O_3 are highly dependent on emissions of O_3 precursors, solar radiation, and other physical processes such as regional and vertical transport (Sun et al., 2018; Ni et al., 2018; Liu et al., 2019; Wang et al., 2016b). While O_3 concentrations show a steady decreasing trend in Europe and North America, an opposite trend with an accelerating increase rate is observed in China (Lu et al., 2018; Li et al., 2019a). Due to high nonlinearity of O_3-NO_x-VOCs relationship and complexity of processes governing ambient levels of O_3, a large uncertainty remains in the determination of impact of different driving factors on changes in surface O_3 concentrations under the polluted atmospheric conditions. Thus, accurate quantification of relative contributions of individual factors to the large increase in surface O_3 concentrations over the heavily polluted regions such as China continues to represent one of major challenges to research communities and government policy makers.

Anthropogenic emissions are the key in driving change in surface O_3. With rapid development of industrialization and urbanization, anthropogenic emissions of NO_x and VOCs, two major precursors of O_3 formation have been increasing significantly in China over the past several decades (Zeng et al.,2019). For instance, tropospheric columns of NO_2 ($TCNO_2$), an indicator of anthropogenic emission intensity of NO_x were increased by 307 % in Beijing from 1996 to 2011 (Huang et al., 2013), which caused a strong

increase trend of O_3 in the lower troposphere. Meanwhile, an increase in surface O_3 at a rate of 2 % a^{-1} was observed in Beijing from 1995 to 2005 (Ding et al., 2007), and a similar increase with 1–2 ppb a^{-1} was monitored at urban and remote sites in eastern China (Sun et al., 2016; Gao et al., 2017; Ma et al., 2016; Tang et al., 2009). However, little light was shed on change in surface O_3 as compared to its counterpart $PM_{2.5}$ which was elevated to the severe pollution level in eastern China especially over the North China Plain (NCP) region (Zeng et al., 2019; Zhai et al., 2019). The severity of $PM_{2.5}$ pollution has been largely alleviated after the stringent emission control strategies were implemented by Chinese governments at national level in 2013 (Zeng et al., 2019). According to the estimate by Multi-resolution Emission Inventory in China (MEIC), anthropogenic emissions of $PM_{2.5}$ decreased by approximately 60 %, NO_x emissions decreased by 21 %, significant reductions were also seen in other air pollutants such as SO_2 but not for VOCs which showed an increase of 2 % instead over the period of 2013–2017 (Zheng et al., 2018). As a result, monthly mean $PM_{2.5}$ concentrations decreased by 41 % for the Beijing-Tianjin-Hebei (BTH) region which is similar to the NCP region presented in this study, and aerosol optical depth (AOD) was reduced by 20 % in eastern China (Li et al., 2019a). However, an opposite trend with an accelerating increase rate of O_3 was observed in the NCP region during this period (Lu et al., 2018; Cooper et al., 2014). The fact that O_3 formation was dominated by VOC-sensitive regime may partly account for such an increase in the NCP region, but it is not clear how much the change of surface O_3 is attributed to anthropogenic emission control efforts.

Aerosol radiative effect is another factor imposing a large constrain on change in surface O_3. Aerosols attenuate surface-reached solar near-ultraviolet (UV) radiation effectively and reduce photolysis rate of NO_2, a key parameter determining O_3 formation. Impact of aerosol radiative effect on photolysis rate of NO_2 or O_3 photochemical production is highly dependent on aerosol optical properties as described by AOD, single-scattering albedo (SSA), and asymmetry factor. AOD is a measure of extinction of solar beam by aerosols (e.g., dust and haze), used as a proxy of representing severity of fine particulate-matter pollution or aerosol mass concentrations. SSA denotes the relative contributions of scattering versus absorption effect to total aerosol extinction efficiency with "0" for pure absorption and "1" for pure scattering effect. Both numerical simulations and observations showed that aerosols with UV-scattering effect may accelerate photochemical production of O_3 but aerosols with strong absorption property (e.g. mineral dust and soot) may inhibit O_3 production in the atmospheric boundary layer (Dickerson et al., 1997; Mok et al., 2016). The lowest photolysis rate coefficient was closely linked with the highest AOD

(Liu et al., 2019; Dickerson et al., 1997). It was observed that surface $PM_{2.5}$ concentrations decreased by 41 % whereas surface O_3 increased at a rate of 3.1 ppb a^{-1} over the BTH region from 2013 to 2017 (Li et al., 2019a). Decrease in $PM_{2.5}$ was considered as one of the important causes leading to such an increase in surface O_3 due to additional O_3 production associated with reduced sink of hydroperoxy radicals (HO_2) (Li et al., 2019a). They pointed out that increase in surface O_3 associated with decrease in $PM_{2.5}$ was more prominent than that with reduction of NO_x emissions over the NCP region where O_3 formation was dominated by VOC-limited regime. Liu and Wang (2020a, 2020b) found the reduction of PM emissions increased the O_3 levels by enhancing the photolysis rates and reducing heterogeneous uptake of reactive gases (mainly HO_2 and O_3), of which the latter is more important than the former. Similar impact associated with aerosol radiative properties on O_3 production was observed in other regions over the world. For instance, the combined effect associated with optical properties of BrC and black carbon (BC) reduced the net change in O_3 production by up to 18 % as compared to BC alone in the Amazon Basin (Mok et al., 2016). Thus, surface O_3 changes are dependent on not only aerosol concentrations (AOD used as a proxy) but also aerosol optical properties such as SSA. Relative importance of different aerosol optical property parameters to change in surface O_3 needs to be addressed.

NCP, the largest alluvial plain of China, is surrounded by Mountains Yanshan with main peak of 2116 meters at the north, Mountains Taihang with the highest elevation of 2882 meters at the west, Mountains Dabie and Tianmu at the south, and bordered to Yellow Sea at the east (see Fig. 1). Such a complex terrain is not conducive to dispersion and dilution of air pollutants and makes them be trapped easily. Meanwhile, the total energy consumption was increased by more than five times from 1985 to 2016 (Zeng et al., 2019). NCP has become one of the most polluted regions in China. The highest $PM_{2.5}$ concentration reached to $900\mu g \cdot m^{-3}$ during winter and heavy $PM_{2.5}$ pollution events was the major concern to air quality during that period (Gu, 2013; An et al., 2019), but surface $PM_{2.5}$ concentrations have reduced substantially. Meanwhile, O_3 exceedance events became more frequent and more serious in the NCP region (Zhang et al., 2015; Lang et al., 2017; Zhai et al., 2019). Hourly surface O_3 concentrations went up to 150.0 ppb and the increase rate reached to 3.1 ppb a^{-1}, much higher than those observed in other polluted regions such as Yangtze River Delta (YRD) and Pearl River Delta (PRD) in China (Li et al., 2019a; Lyu et al., 2019). The elevated surface O_3 has become an emerging critical air quality issue in this region (Wang et al., 2006; Shi et al., 2015). Understanding of the factors driving such as a rise in surface O_3 becomes a very hot topic (Li et al., 2019a; Li et al., 2019b). However, most of the related studies are

limited to the contributions of atmospheric chemistry and changes in O_3 precursors' emissions. Relative importance of aerosol radiative effect associated with substantial decrease in aerosols or $PM_{2.5}$ and meteorological variability to the enhancement of surface O_3 is not well qualified.

In this study, seven-year air quality observational data provided by the China National Environmental Monitoring Center (CNEMC) Network are examined to determine the temporal and spatial variations in surface O_3 over the NCP region over the period of 2013–2019. A series of analyses are presented to investigate the long-term change trend of surface O_3 and the statistical relationships with NO_x and VOCs emissions, meteorological variables, and aerosol radiative optical property parameters. A box model with Master Mechanism (MM) then is utilized to determine the response of surface O_3 to the key driving factors. The specific objectives include 1) to identify the key factors driving the increase in surface O_3 over NCP, the most polluted region in China; 2) to quantify the relative contributions of anthropogenic emissions (e.g., NO_x and VOCs), aerosol concentrations, aerosol optical properties, and meteorological variability to the increase in surface O_3 in summertime during 2013–2019.

2 Data and Methods

2.1 Observational data

Data used in this study include hourly-averaged surface observations of O_3 and $PM_{2.5}$ from 2013 to 2019 provided by the CNEMC (http://106.37.208.233:20035/). UV data measured at the Yucheng site (i.e., YCA, 116.57° E, 36.87° N) in the NCP region are obtained from the Chinese Ecosystem Research Network (http://www.cern.ac.cn/) from years 2013 to 2016. AOD is derived from the monthly level-3 product of the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument aboard the Aqua satellite, reported at 550-nm wavelength with resolutions of 1° × 1° (Platnick, 2015). $TCNO_2$ data are retrieved from the daily level-3 products of the Ozone Monitor Instrument (OMI) aboard the Aura satellite with resolutions of 0.25° × 0.25° (Nickolay A. Krotkov, 2019). Short-wave radiation data are provided by Land Data Assimilation System (FLDAS) (NASA, 2018) at resolutions of 0.1° × 0.1°. SSA retrieved from OMI/Aura Near UV Aerosol Optical Depth and Single Scattering Albedo V003 (OMAERUV) (Torres, 2006) at 388 nm are used to evaluate the impact of aerosol scatting/absorption properties on change in surface O_3. Daily max temperature at 2 m (T_{2max}), 10 m wind speed and the planetary boundary layer height (PBLH) are derived from the Modern-Era Retrospective Analysis for

Research and Applications version 2 (MERRA-2) reanalysis data at horizontal resolutions of 0.5° × 0.625° (Global Modeling and Assimilation Office, 2015).

2.2 Model description and configurations

The MM model is utilized to quantify the relative contributions of anthropogenic emissions and aerosol optical and radiative properties to the change in surface O_3. The MM is a chemistry box model, originally developed and updated by the scientists at National Center for Atmospheric Research (NCAR). It includes a detailed and flexible gas phase chemical mechanism consisting of approximately 5000 reactions for simulating temporal variations in chemical species of interest. The hydrocarbon chemistry in the MM is treated explicitly with photo-oxidation of partly oxygenated organic species included. Alkanes, alkenes and aromatics are considered as initial hydrocarbon reagents in the gas-phase mechanism. The Gear-type solver is used in the MM model to handle so large numbers of chemical reactions and species and the integration time steps varied during the simulations (Madronich and Calvert, 1989). The TUV model is called by the MM model for update of chemical reaction rates every fifteen minutes. This model computes time-dependent chemical evolution of an air parcel initialized with a known composition and additional emissions. It is assumed that no dilution is included in the simulations given the difficulty of getting inputs to calculate the dilution rate. The transport in and out of air pollutants reached a quasi-equilibrium state over the study domain and no heterogeneous processes was included in the MM model. The MM model has been widely used to investigate impact of different factors such as emissions, chemistry, and meteorological conditions on simulations of O_3 and other chemical species (e.g., Liu et al., 2019; Geng et al., 2007).

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Photolysis rate j(NO_2) is calculated by using the Tropospheric Ultraviolet and Visible (TUV) radiation model which is embedded into the NCAR MM (Madronich S., 1999). In the fully-coupled system, the TUV is called by the MM model for update of photolysis rates of NO_2 and other chemical species (e.g., H_2O_2, O_3, NO_3, N_2O_5) every 15 minutes dynamically. The TUV model is initialized with the monthly means of AOD, SSA, and total columns of O_3 retrieved from satellite measurements as well as other meteorological parameters such as cloud fractions at the central point of NCP (36° N, 117.5° E) in June.

HO_2 radicals are important to O_3 formation. The HONO photolysis as the primary production of OH radicals and the formaldehyde (HCHO) photolysis as the net radical source of HO_2 can lead to major

changes in the HOx and NOx budget that may have an important effect on O_3 production and loss (e.g., Aumont et al., 2003; Brasseur et al., 2006; Lin et al., 2012a). The role of HO_2 radicals can be determined by the following reactions.

$$HO_2 + NO \rightarrow NO_2 + OH, \quad \text{R1}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P), \quad \text{R2}$$

$$O_2 + O(^3P) \rightarrow O_3, \quad \text{R3}$$

where $h\nu$ represents ultraviolet radiation at the wavelengths of 200–400 nm. The MM model has a capability of quantifying the role of radicals in O_3 formations under different pollution conditions.

The MM simulations are conducted for the predefined box as shown in Fig. 1 to represent ensemble mean behaviors and responses of the model to changes of different model inputs over the NCP region. The 24-hr simulations are conducted with the initial hour at 00z local time (LT). The inputs of the simulations include meteorological data (e.g., air temperature, cloud, and PBLH), aerosol radiative properties (i.e., AOD and SSA), and emissions. While all the meteorological inputs are generated from observational data, the initial values of chemical species such as VOC species (e.g., Acrylic, 2-methylbutane, Toluene, P-xylene, Isoprene), N_2, O_2, H_2O, NO_2, O_3 etc. are obtained from climatology or background values.

Emissions (NO_x and VOCs) are calculated from the MEIC emission inventory. Aerosol radiative property parameters from MODIS and OMAERUV are assumed as constants for all the simulations. All the simulations are driven by the monthly means averaged over the entire NCP region. The temporal variations at an interval of 4 hours are included in the model inputs to represent the diurnal variations in different meteorological variables such as T_{2max} and PBLH from MERRA-2 reanalysis.

Six groups with a total of sixteen numerical experiments with the MM model are designed to quantify the roles of different factors in driving change in O_3 concentrations (Table 1). Case A stands for the base that the emissions were generated from MEIC in base year 2012 (http://www.meicmodel.org/) with an adjustment for year-2013 use, and the spatial distributions of NO_x and VOCs are presented in Fig. S1. Case B represents a scenario for year 2019 with NO_x and VOCs emission changes by − 35 % and + 10 % with respect to the case in year 2013, respectively. The changes in NO_x emissions (− 35 %) and VOCs emissions (+10 %) in 2019 were obtained by extrapolating their respective changes during the period from 2013 to 2017 (Li et al., 2019a). Case C1 denotes a scenario with AOD decreased from 1.0 (i.e., the

case for year 2013) to 0.75 (i.e., for year 2019) according to MODIS measurements and other six members in group C are used to examine the impact of varying AOD on the change in surface O_3. Case D1 is the one with a change of SSA from 0.95 (year 2013) to 0.93 (year 2019). Case E is a scenario with T_{2max} increase from 29.9 ºC in 2013 to 32.0 ºC in 2019 based on regional average calculated with the MERRA-2 reanalysis in the NCP region. Case F is designed to assess the impact of the increased PBLH (i.e., increase from 0.76 km in 2013 to 0.97 km in 2019) on surface O_3 change in the NCP region. Case G is for the situation mimic for year 2019 representing the combined effect of changes in emissions, AOD, SSA, T_{2max}, and PBLH. 24-hr simulations are completed for each case to quantify the contributions of individual factors to the changes in surface O_3 from 2013 to 2019. More details of the numerical experiments are presented in Table 1.

3 Results and Discussion

3.1 Spatiotemporal variations in surface O_3, $PM_{2.5}$, AOD, and $TCNO_2$

Figure 2 shows a comparison of spatially distributed monthly means of the maximum daily 8-h average (MDA8) O_3, 24-h average $PM_{2.5}$, AOD, and $TCNO_2$ over the eastern China in June between 2013 and 2019 derived from in-situ and satellite observations. It is clear that NCP was the most polluted region with the highest values of MDA8 O_3, $PM_{2.5}$, AOD, and $TCNO_2$ over the past decade. 24-h average $PM_{2.5}$ concentrations were higher than 75.0 $\mu g\, m^{-3}$ (the Grade II National Ambient Air Quality Standard, NAAQS defined for residential areas) at most of the monitoring stations across the NCP region in June 2013. The highest 24-h average $PM_{2.5}$ reached to 766.0 $\mu g\, m^{-3}$ and the corresponding AOD was 1.0. As compared to the well-established monitoring network of $PM_{2.5}$, observational sites for O_3 were pretty sparse except for the BTH, YRD, and PRD across the eastern China in 2013. While the $TCNO_2$ was 2 times higher than that observed in North America (Stavrakou et al., 2008), the exceedance events of the MDA8 O_3 were not frequently observed across eastern China in 2013. $PM_{2.5}$ was the major air pollutant in the NCP region during that time period.

$PM_{2.5}$ concentrations, AOD, and $TCNO_2$ have been reduced substantially as a result of the implementation of strict anthropogenic emission reduction policy in 2013. For instance, monthly mean of $PM_{2.5}$ concentrations decreased from 95.5 $\mu g\, m^{-3}$ to 33.2 $\mu g\, m^{-3}$ with a percentage reduction of 65 %. Monthly mean AOD was reduced from 1.0 in 2013 to 0.75 in 2019, indicating that $PM_{2.5}$ continued

to decrease at a rate of $-10 \sim -11$ % a^{-1} which was similar to that during 2013–2017 (Li et al., 2019a). On the other hand, a rapid increase in surface O_3 concentrations was observed in the NCP region over the past several years. The hot spots with the MDA8 O_3 higher than 75.0 ppb were extended to the entire NCP as well as the neighbor regions in 2019 (Fig. 2b). The highest MDA8 O_3 reached to 112.8 ppb in 2018, which was even higher than the level (110.0 ppb) observed in Los Angeles (Lin et al., 2017). As compared to the cases observed in 2017 (Li et al., 2019a; Li et al., 2019b), air pollution events with higher surface O_3 became more severe and more frequent. The frequency of NAAQS exceedance events for surface MDA8 O_3 (i.e., greater than 160 $\mu g\, m^{-3}$) in June increased from 30 % in 2013 to 63 % in 2019. Here percentage represents the proportion of MDA8 exceedance days to a total of 30 days (i.e., June).

Reduction in NO_x emissions and slight increase in VOC emissions could be part of the reasons causing such an increase over the NCP region where O_3 formation was dominated by VOC-limited regime. To better understand the relationship of increase in surface O_3 with the decrease in NO_2, the change in monthly mean Ox (a sum of O_3 and NO_2) was plotted in Fig. S2. It is clear that Ox showed an increasing trend over the past 7 years during daytime and nighttime in both urban Beijing and the NCP region. Meanwhile, Li et al. (2019a) attributed the increase to aerosol chemistry that removal of HO_2 radicals was reduced and more O_3 production was promoted. On the other hand, attenuation of UV radiation became less evident as $PM_{2.5}$ or AOD continually decreased. Strengthening UV radiation may accelerate photolysis of NO_2 and eventually led to more O_3 production. Importance of aerosol radiative effect in the increase in surface O_3 via the way of accelerating photolysis of NO_2 can be further evaluated through numerical experiments.

Meteorological conditions are another critical factor affecting O_3 production. Typically, higher air temperature is responsible for higher photochemical reaction rates and more O_3 photochemical production (Porter and Heald, 2019). As shown in Fig. 3, NCP was the hottest spot region with T_{2max} which was about 4.0 °C higher than that in the neighbor regions. In addition, increase rate of T_{2max} in the NCP was larger than that observed in other regions in eastern China. T_{2max} and surface-reaching shortwave radiation increased by 3 % and 7 %, respectively, over the past several years. In addition to man-made factors such as urbanization and industrialization, decrease in aerosols (e.g., $PM_{2.5}$ and AOD) could be an important factor driving such a rise in air temperature due to weakening aerosol radiative effect.

3.2 Yearly changes in surface O_3 during 2013–2019 and driving factors

As presented above, NCP was the most polluted region with extremely high ambient levels of air pollutants. Surface O_3 showed a rapid increase over the period from 2013 to 2019 while $PM_{2.5}$ and other pollutants such as NO_x experienced a significant reduction. O_3 has become a major air quality concern in summer. June was the month with the highest monthly mean MDA8 O_3 concentrations (Fig. S2). In this section, we attempt to investigate the yearly change rate and to identify the factors that drove such a large increase in surface O_3 over the NCP region throughout the period of 2013-2019.

Figure 4 shows the yearly changes in monthly means of MDA8 O_3, $PM_{2.5}$, AOD, SSA, $TCNO_2$, T_{2max}, and PBLH over the NCP region in June from 2013 to 2019. The change in monthly mean of surface MDA8 O_3 showed an opposite trend to that of $PM_{2.5}$ concentrations and other air pollutants. The increase rate of monthly mean MDA8 O_3 (4.6 ppb a^{-1}) during 2013–2019 was much higher than that observed in the same region during the period of 2005–2015 (1.1 ppb a^{-1}) (Ma et al., 2016), and other regions such as Mountain Tai, YRD, Hong Kong, and North America where the changes were less than 2.1 ppb a^{-1} during the similar time period (e.g., Sun et al., 2016; Gao et al., 2017; Wang et al., 2017; Xu et al., 2019). At the same time, a large decrease can be found from the time series of $PM_{2.5}$, AOD, and $TCNO_2$. It is noted that SSA also showed a decreasing trend (Fig. 4e). Decrease in SSA was likely due to the fact that reduction of inorganic aerosols (e.g., sulfate and nitrate) was larger than that of carbonaceous ones (Zhang et al., 2020). Another noticed feature is that MDA8 O_3 showed a decreasing trend in 2019 relative to 2018, which was opposite to that during 2013–2018 (Fig. 4a). It is worth to witness the change trend in the coming years.

To understand the factors driving the change in surface O_3, a series of scatter plots are presented to examine the relationships between the surface MAD8 O_3 and individual factors such as aerosol optical properties (i.e., AOD and SSA), $TCNO_2$, T_{2max}, and surface-reaching short-wave radiation over the past seven years in June (Fig. 5). The values discussed here represent the monthly means. MAD8 O_3 showed two different regimes with an opposite dependence of O_3 formation on $PM_{2.5}$ concentrations. The first regime showed a decrease trend with increasing surface $PM_{2.5}$ when $PM_{2.5}$ concentrations were less than approximately 140.0 $\mu g\, m^{-3}$ whereas the second one showed no trend with increasing $PM_{2.5}$ when $PM_{2.5}$ concentrations were higher than 140.0 $\mu g\, m^{-3}$. The first regime was highly related to aerosol radiative effect, which has been discussed above. For the 2nd regime, the impact of aerosol radiative effect

on surface O_3 photochemical production seemed very minor or even negligible. Instead, O_3 production was suppressed significantly and MAD8 O_3 concentrations were less than 20.0 ppb. In this case, removal of surface O_3 through titration of NO was not effective and surface O_3 showed an increase rather than a decrease trend with increasing NO_x concentrations under the strong NO_x conditions as indicated by $TCNO_2$ higher than 40–45$\times 10^{15}$ (cm^{-2}) in the troposphere. Here the threshold value of 140.0 $\mu g\, m^{-3}$ represents an observed reality in this region but it needs to investigate whether such a threshold value exists in other regions.

Figures 5d–e further demonstrate the critical role of meteorological factors in change of surface O_3. MDA8 O_3 showed a near linear increasing trend with increasing T_{2max} and surface-reaching shortwave radiation with respective linear regression correlation coefficients of 0.88 and 0.93. Increase in T_{2max} and strengthening shortwave radiation caused by decrease in $PM_{2.5}$ (a proxy of aerosols) played a positive role in driving the increase in surface O_3 in the NCP region. On the other hand, MDA8 O_3 showed a decrease trend with 10 m wind speed (Fig. 5f). That may explain why improvement of stagnation atmospheric conditions may alleviate severity of surface O_3 pollution to some extents. The positive correlation between the PBLH and O_3 shown in Fig. 5g represents one case when radiation is stronger and temperature is higher, that are favorable for O_3 formation. Meanwhile, higher PBLH could enhance the transport down of O_3-enriched air aloft, resulting in an increase in surface O_3 (Reddy et al., 2012). On the other hand, some studies found a negative correlation between the PBLH and O_3. They claimed that a shallower PBL may suppress the dispersion of pollutants and lead to higher O_3 (Yan et al., 2018; Jiang et al., 2016; Wei et al., 2016; Huang et al., 2005)

Enhancement of UV radiation resulting from reduction in surface $PM_{2.5}$ represents one of important mechanisms in driving increase in surface O_3 concentrations. It can be further illustrated by Fig. 6. While UV radiation displays a nonlinear decreasing trend with surface $PM_{2.5}$ concentrations, surface O_3 (hourly) shows a near linear increasing trend with surface-reached UV radiation. UV radiation attenuation approaches to a constant with a value of 0.1–0.3 MJ m^{-2} when surface $PM_{2.5}$ concentrations reach to around 300 $\mu g\, m^{-3}$ or above.

Analyses presented above demonstrate that all the exceedance events of MDA8 are observed under conditions with $PM_{2.5}$ less than 60 $\mu g\, m^{-3}$, $TCNO_2$ of equal to or less than 5.0 $\times 10^{15}$ (cm^{-2}), T_{2max} higher than 28.0 °C, and surface-reaching shortwave radiation stronger than 250.0 W m^{-2}. Reduction in aerosols (e.g., surface $PM_{2.5}$ as a proxy) concentrations may strengthen UV radiation, increase T_{2max}, and

eventually promote more surface O_3 production.

3.3 Relative contributions of different driving factors to increase in surface O_3

In this section, the box model MM is utilized to quantify the relative contributions of individual driving factors to the increase in surface O_3 over the NCP region during 2013–2019. A simulation-observation comparison is presented to evaluate the performance of the MM model on simulations of surface O_3 (Fig. 7), of which the O_3 observations averaged over all the stations in NCP is considered as the standard observed concentrations. The simulated O_3 peak was about one hour later than the observation, which was likely due to uncertainty of emission inventory and other meteorological factors. Overall, the MM model was able to mimic the observed variation pattern and peak value as indicated by the correlation coefficient of 0.95 between simulated and observed O_3.

A series of numerical experiments were then completed with the MM model to quantify the relative contributions of anthropogenic emissions (i.e., NO_x and VOCs), AOD, SSA, air temperature, and PBLH to the change in surface O_3 over the NCP region during 2013–2019. The results are presented in Table 2. The changes in emissions of O_3-precursors (i.e., NO_x and VOC_s) (i.e., Case B) and decrease of AOD (i.e., Case C1) were the two major contributors with their respective positive contributions of 45 % and 70 % to the increment in surface O_3. But increase in surface O_3 associated with AOD reduction was largely offset by the reduction in SSA. Moreover, air temperature played a non-negligible role and the increase in T_{2max} accounted for 12 % of surface-O_3 enhancement (Case E). Meanwhile, the increase of PBLHs also contributed about 18 % to the increment in surface O_3 (Case F). As indicated by Case G, the combined effect by multiple factors was larger than the simple summation of individual factor's contributions or the total percentage contributions by individual factor was less than 100 %. This is likely due to the fact that O_3 production is not the linear function of individual factor's contribution. Complex interplay among different factors may account for rest of the increase (i.e., 2 %).

It is not surprised that reduction in NO_x emissions brought about increase in surface O_3 since O_3 formation was dominated by VOC-limited regime in most parts of the NCP region. Several numerical experiments were conducted to understand the mechanism of reduced $PM_{2.5}$ or AOD facilitating the increase in surface O_3. It is known that photolysis rate of NO_2, j(NO_2) plays a critical role in O_3 formation. Parameter j(NO_2) was highly dependent on aerosol optical properties such as AOD and SSA, as well as

solar zenith angle (θ) (Dickerson et al., 1997). As shown in Fig. 8a, decreasing AOD was conducive to photolysis of NO_2 due to reduction of attenuated UV radiation entering the PBL. However, weakened scattering or strengthened absorption property of aerosols (i.e., reduced SSA) may attenuate the UV entering the PBL, deaccelerating photolysis of NO_2. Thus, decrease in SSA may counteract the impact associated with decrease in AOD, which may slow down the increase in surface O_3 to some extents. In addition, j(NO_2) showed the highest value at noontime ($\theta = 0°$ or $\sec\theta = 1$) and tended to decrease when θ became larger (i.e., early morning or late afternoon). Figure 8b further demonstrates that O_3 formation or MDA8 O_3 showed a near linear increasing trend with j(NO_2). While decrease in $PM_{2.5}$ concentrations or AOD strengthened the UV amount entering the PBL reduction in SSA may counteract impact of decreased AOD partially. But impact of AOD outpaced that of SSA. Thus, surface O_3 (e.g., MDA8 O_3) still showed a large increase with the combined effect of AOD and SSA over the past several years.

Now let us turn our attention to O_3-chemistry in the varying polluted region. As illustrated in Fig. 9, HO_2 radicals were sensitive to aerosol properties (i.e., AOD and SSA) but the sensitivity was highly relied on the solar zenith angle (θ). HO_2 radical was more sensitive to AOD or SSA in the afternoon than in the morning while photolysis rate of HO_2 is more sensitive to AOD or SSA. It is noted that higher net O_3 production is highly associated with the faster decrease in J(O_3) than J(NO_2) in the afternoon (Gerasopoulos et al., 2006). HO_2 radical abundance reduced as aerosol optical property became more absorptive. This indicates that decrease in SSA may cause reduction of HO_2, less NO_2, and then less O_3 production. The HO_2 peak hour was matched well with that of O_3 peak (around 15 p.m. LT), further confirming its important role in O_3 formation. Decrease in AOD may accelerate production of HO_2 radicals or slow down their sink, which was conducive to production of NO_2 (Li et al., 2019a) but decrease in SSA may offset its impact if aerosols show strong absorption property. Meanwhile, strengthened UV associated with weakened aerosol radiative effect was conducive to photolysis of NO_2. As a result, more O_3 is produced. This accounted for substantial increase in surface O_3 while $PM_{2.5}$ decreased over the past several years (2013 to 2019). The results are consistent with the finding by Li et al. (2019a).

4 Discussions

In this study, a box model NCAR MM with the detailed NO_x-VOC-O_3 chemistry included is utilized to quantify percentage contributions of emissions, aerosol optical properties, and meteorological variabilities to increase in surface O_3 over the NCP region during 2013–2019. The findings may provide more scientific evidence to policy makers on developing more effective control strategies on reduction in ambient levels of O_3 as well as exceedance events. However, three points deserve further discussions.

First, the impact of aerosol radiative effect on surface O_3 formation is dependent on not only aerosol abundance (i.e., AOD) but also aerosol scattering/absorption property (i.e., SSA). Their impacts can be offset to some extents when AOD and SSA show the same change trend (either increase or decrease) or can be strengthened substantially when both AOD and SSA show an opposite change trend. Here the study on the NCP region represents the first case since both AOD and SSA showed a decrease trend over the past several years. Even so, the combined impact of aerosol radiative effect due to reductions in AOD and SSA still contributed 23% of the total change in surface O_3 in the NCP over the past several years. This reminds us that the impact of aerosol radiative effect could be more substantial if both AOD and SSA show an opposite change trend. Moreover, as compared to impact of change in AOD on surface O_3 formation (e.g., Dickerson et al., 1997; Wang et al., 2016a; Xing et al., 2015; Xing et al., 2017), studies on impact of change in SSA on surface O_3 formation are fewer (Dickerson et al., 1997; Mok et al., 2016). Thus, changes of individual aerosol radiative property parameters must be addressed carefully in order to present more accurate quantification of impact of aerosol radiative effect on change in surface O_3.

Second, as presented above, the MM model as a box model with the detailed O_3-NO_x-VOCs relationship allows us to quantify relative contributions of individual factors to increase in surface O_3. Overall, the model results are comparable to those by using three-dimensional (3D) chemistry and transport models (e.g., Liu and Wang 2020a, 2020b). The MM model indicates that reduction of anthropogenic emissions of NO_x was the greatest contributor (45 %) to the increase in surface O_3 in the NCP region during 2013–2019, which was larger than Li et al., (2019a) in summertime from 2013 to 2017 (about 10 %) but less than that of Sun et al. (2019) in July from 2003 to 2015 (63 %) over the eastern China. This represents the preponderant role of NO titration. Lower NO emissions destroy less ozone, which in most stations is originated from the tropospheric/boundary layer background. Aerosol radiative effect was ranked as the 2nd contributor to the change in surface O_3 in this region. The percentage

contribution was found to be larger than that presented by other studies (Li et al., 2019a; Xing et al., 2015). This is partly because this study is focused on the impact on MDA8 O_3 whereas their studies investigated the impact on diurnal variations of surface O_3. In addition, Li et al., (2019a and 2019b) and Liu and Wang (2020a and 2020b) pointed out that aerosol chemistry played the most important role in the enhancement of surface O_3 in this region through modification of HO_2 radicals that produce additional O_3 formation. However, the MM model does not include aqueous-phase chemistry that has been implemented in the 3D meteorology/chemistry models (e.g., Li et al., 2019a; Liu and Wang, 2020a, 2020b). Thus, inclusion of detailed aerosol chemistry and observation-based uptake coefficients in a box model like MM is necessary to provide more accurate assessment of impact of aerosol radiative effect on surface O_3 change.

Third, as compared to 3D meteorology/chemistry coupling model(s), box model does not include complex physical processes such as regional transport, vertical diffusion, and cloud formation, etc. The influence of changing meteorological factors on the change trend in surface O_3 may vary greatly with regions and time. In addition to air temperature and the boundary layer conditions, other meteorological factors such as cloud cover, precipitation, wind fields played an important role in driving the changes in surface O_3 observed in many places of China (Liu and Wang, 2020a). Computational resource and workload that a box model requires are much less than that a 3D chemical transport model needs. This may allow us to complete a series of designed numerical experiments to quantify the roles of individual factors easily with limited computational resources. It is acceptable by using a box model if terrains are relatively flat in the box, horizontal gradients of emissions and air pollutant concentrations are not strong, and transport in and out reaches a relative equilibrium state. As shown in Fig. S1 and Fig. 2, the NCP region defined in this study represents the most polluted part in eastern China, anthropogenic emissions tend to distribute relatively uniform across the region. To this extent, it is appropriate to examine O_3 formation and its response to changes of different factors such as emissions, meteorological conditions, and aerosol radiative properties by using a box model in the NCP region. It is reminded that some other factors such as background ozone are not included in our sensitivity study due to their limited impact in this region, and the box model results present an ensemble-mean behavior for the given box but need further evaluations by using a complex meteorology/chemistry coupling model such as Weather Research and Forecasting model with Chemistry (WRF/Chem). Besides, the change in tropospheric O_3 could exert an important impact on ozone in the atmospheric boundary layer (ABL) or near surface. For instance,

Jiang et al. (2015) presents an O_3 episode in the southeast costal of China, and found that the downward transport of O_3 from the UTLS region driven by a typhoon is the key factor causing a large increase in surface O_3 by 21-42 ppb. East Asia including the NCP region is considered as a net export region of O_3 from the ABL rather than an import (e.g., Cooper et al., 2010; Lin et al., 2012b). On the other hand, the long-range transport of O_3 from Africa may exert an important impact on O_3 peaks in Asia around 25^0N, i.e., the south of our study area, NCP (32^0N-40^0N), with the largest impact in boreal winter and early spring (>10 ppb) and the lowest in boreal summer (<6ppb) (Han et al., 2018; Gaudel et al, 2018). The impact of tropospheric O_3 should be taken into account when the observational data are available in NCP region.

Forth, that synoptic pattern may exert an important impact on tropospheric and surface O_3 concentrations. For instance, high concentrations of surface O_3 or O_3 episodes occurred in western Mediterranean and central Europe were usually linked with anticyclone synoptic pattern which led to a large-scale subsidence, clear sky, and high temperature (e.g., Kalabokas et al., 2013; Kalabokas et al., 2017). Yin et al. (2019) concluded that synoptic patterns played a critical role in summer ozone pollution in eastern China. Under the control of zonally enhanced East Asian deep trough, the local hot, dry air and intense solar radiation enhanced the photochemical reactions and produced more O_3. The inter-annual magnitude variations of the domain synoptic patterns may have an important impact on surface O_3 episodes, and its impact on the long-term changes needs a further investigation.

5 Summary and conclusions

In this study, seven-year long surface observational air quality data are presented together with satellite retrieval measurements of $TCNO_2$, AOD and SSA to investigate long-term change trend of surface O_3 over the NCP region in summer from 2013 to 2019. A comprehensive statistical analysis is completed to explore the relationship of MDA8 O_3 with $PM_{2.5}$ concentrations, tropospheric columns of NO_2, AOD, and meteorological variables such as T_{2max}, surface-reaching shortwave radiation, wind speed, and PBLH. A box model representing the O_3-NO_x-VOCs relationship is then utilized to quantify the relative contributions of different driving factors to the increase in surface O_3 in the NCP region over the period of 2013–2019.

The observational analysis indicates, while $PM_{2.5}$ concentrations continued to decrease with a rate of

9.5 $ug\ m^{-3}\ a^{-1}$, surface O_3 showed an accelerated increase trend at a rate of 4.6 ppb a^{-1} over the NCP region during summertime from 2013 to 2019. Both decrease in $PM_{2.5}$ and reduction in $TCNO_2$ are the two key factors leading to such an increase in surface O_3. The former is closely associated with the attenuation of UV entering the PBL whereas the latter is related to the fact that O_3 photochemical production in the NCP region is dominated by VOC-limited regime. The trend analysis of satellite retrieval measurements revealed an obvious increase in T_{2max} at the rate of 0.34 $^oC\ a^{-1}$, a rapid decrease in AOD from 1.0 in 2013 to 0.75 in 2019, and a reduction in SSA from 0.95 to 0.93. The changes of both T_{2max} and AOD were conducive to photochemical production of O_3 whereas the variability of aerosol scattering/absorption property (i.e., decrease in SSA) may largely offset the impact of AOD reduction.

The sensitivity studies with the box model MM indicate that reduction of emissions (i.e., NO_x), meteorological conditions, and aerosol radiative effect associated with decrease in aerosol concentrations were the three most important factors in driving such a large increase in surface O_3. They accounted for 45 %, 30 %, and 23 % of the total increase in surface O_3, respectively over the NCP region in summertime during 2013-2019. For the meteorological contribution, increases in the PBLH and air temperature (e.g., T_{2max}) were responsible for 18 % and 12 % of the total change of surface O_3, respectively. The percentage contribution of aerosol radiative effect (23 %) represented the net changes caused by aerosol concentrations (i.e., AOD) and aerosol radiative property (scattering/absorption, SSA) (70 % vs. − 47 %). The model results further demonstrated that decrease in SSA (i.e., more absorptive) may lead to reduction in HO_2 radicals and NO_2 concentrations, and then less O_3 production, which may largely counteract impact of aerosol radiative effect associated with decrease in AOD.

This study has a strong implication that development of more effective control strategies on surface O_3 reduction needs to consider impact of aerosol radiative effect as well as the change of aerosol scattering/absorption properties (i.e., AOD and SSA).

Data availability: Data used in this paper can be provided by Xiaodan Ma (xaiodanma_nuist@163.com) upon request.

Author contributions: JH came up with the original idea of this study. XM and JH designed the numerical simulations. XM conducted the data analysis and the first draft of manuscript and JH did the

edit work. TZ, CL, KZ, JX and WX were involved in the scientific interpretation and discussions. All the authors commented on the paper.

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730 **Table 1.** A summary of numerical experiments with the NCAR MM model.

Case	NOx emission	VOCs emission	AOD	SSA	T_{2max} (ºC)	PBLH (km)
A	2013*	2013*	1.0	0.95	29.9	0.76
B	**2019**+	**2019**+	1.0	0.95	29.9	0.76
C1	2013	2013	**0.75**	0.95	29.9	0.76
D1	2013	2013	1.0	**0.93**	29.9	0.76
E	2013	2013	1.0	0.95	**32.0**	0.76
F	2013	2013	1.0	0.95	29.9	**0.97**
G	**2019**	**2019**	**0.75**	**0.93**	**32.0**	**0.97**
C2	2013	2013	**0.5**	0.95	29.9	0.76
C3	2013	2013	**0.6**	0.95	29.9	0.76
C4	2013	2013	**0.7**	0.95	29.9	0.76
C5	2013	2013	**0.8**	0.95	29.9	0.76
C6	2013	2013	**0.9**	0.95	29.9	0.76
C7	2013	2013	**1.1**	0.95	29.9	0.76
C8	2013	2013	**1.2**	0.95	29.9	0.76
C9	2013	2013	**1.25**	0.95	29.9	0.76
D2	2013	2013	1.0	**0.94**	29.9	0.76

*Year 2013: NO_x emission is 2.0×10^{12} mole. $cm^{-2}\,s^{-1}$, and VOCs emission is 7.3×10^{9} mole. $cm^{-2}\,s^{-1}$

+Year 2019: NO_x emission is 1.3×10^{12} mole. $cm^{-2}\,s^{-1}$, and VOCs emission is 8.0×10^{9} mole. $cm^{-2}\,s^{-1}$.

735

Table 2. Relative percentage contributions of emissions (case B), AOD (case C1), SSA (case D1), air temperature (case E), and PBLH (case F) to the change in MDA8 O_3 over the NCP region during 2013–2019.

	MDA8 O_3 (ppb)	Concentration Change (ppb)	Percentage Change (%)	Percentage Contribution (%)
A	55.35			
B	59.25	3.90	+ 7 %	+ 45 %
C1	61.46	6.11	+ 11 %	+ 70 %
D1	51.22	− 4.13	− 7 %	− 47 %
E	56.43	1.08	+ 2 %	+ 12 %
F	56.95	1.60	+ 3 %	+ 18 %
G	64.09	8.74	+ 16 %	

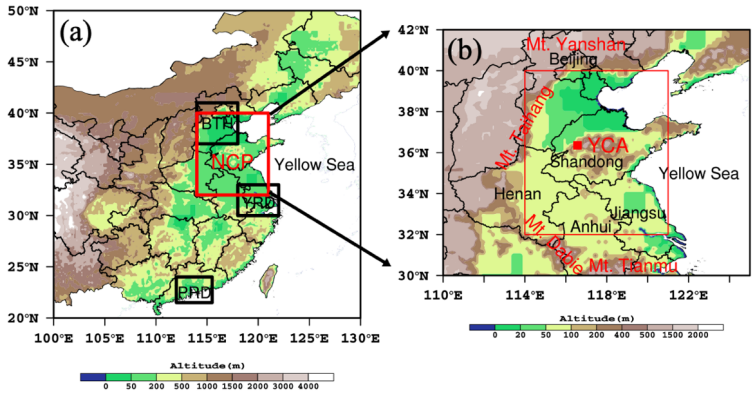
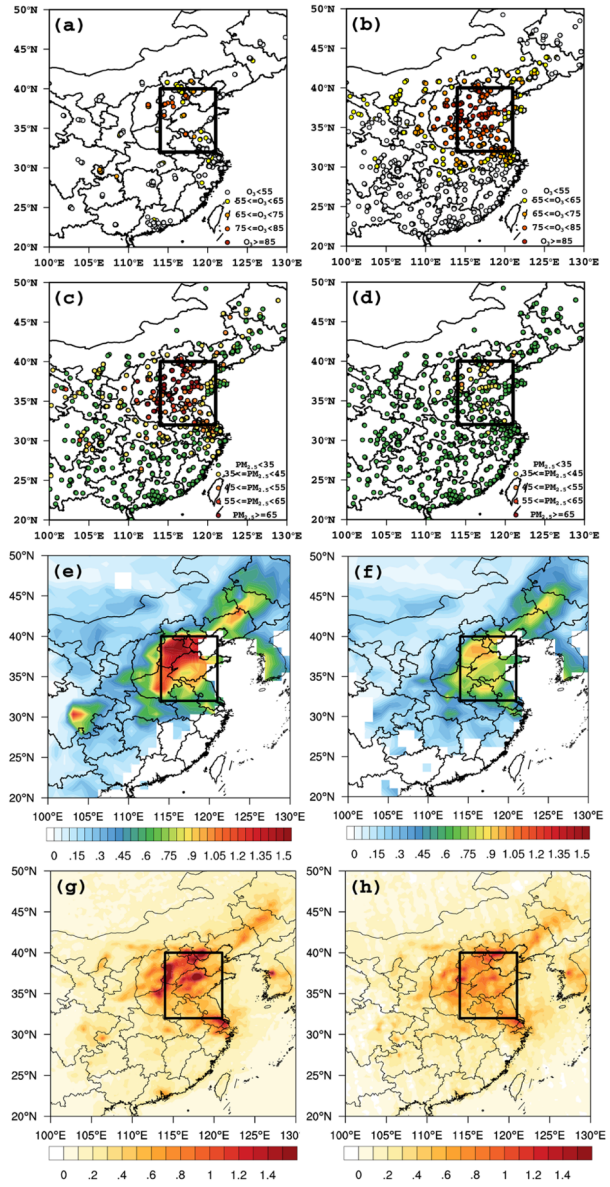
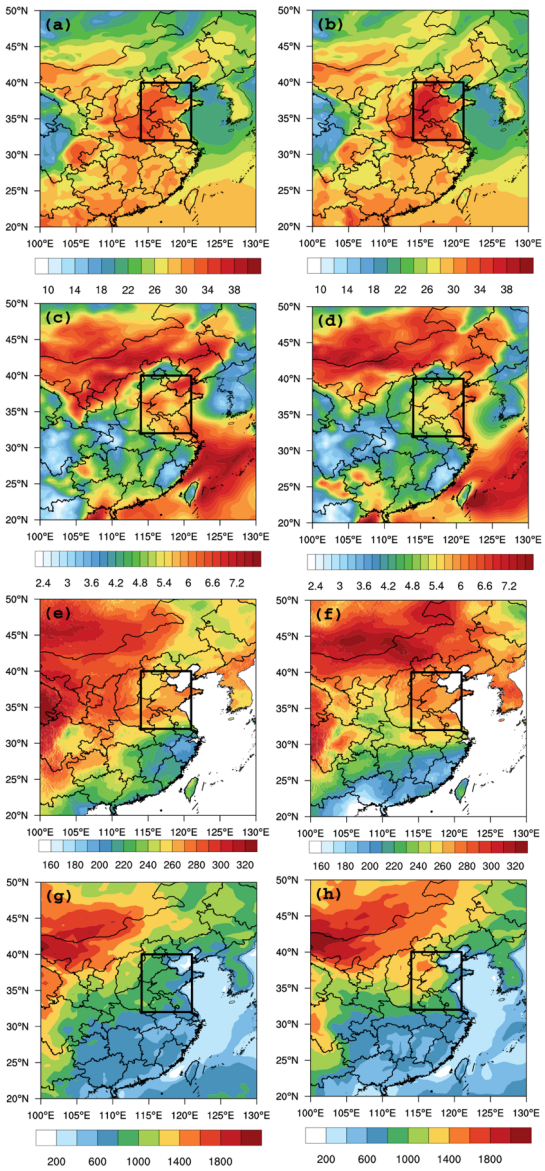


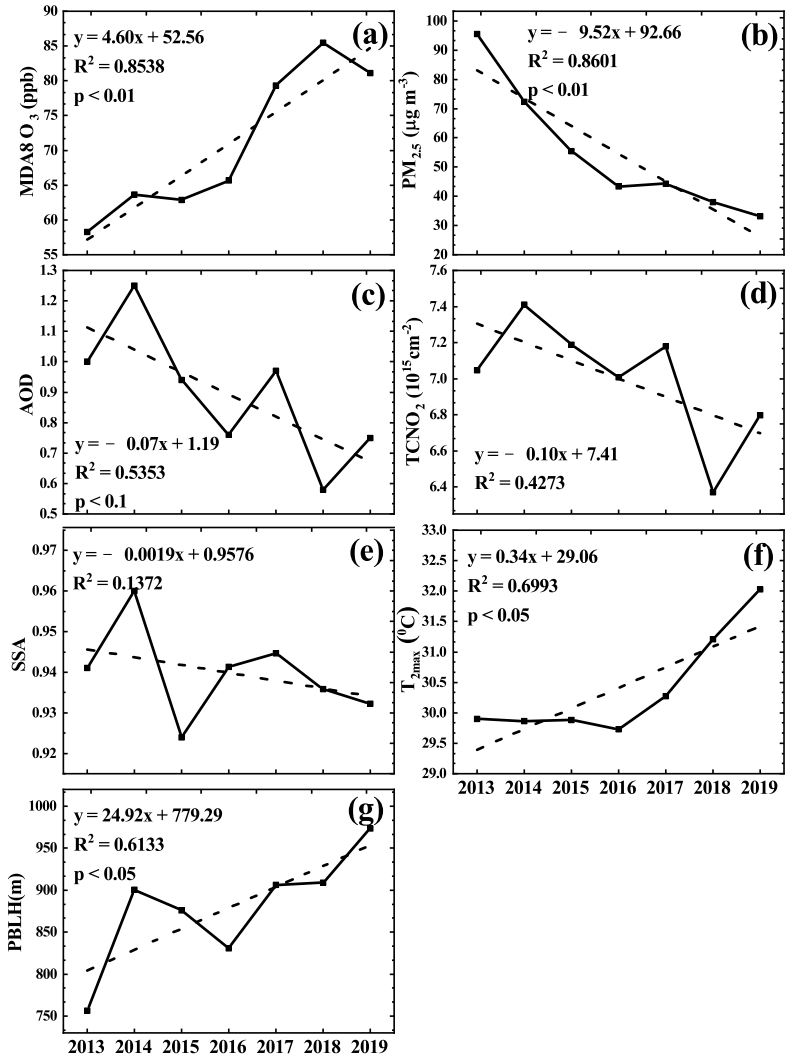
Figure 1. (a) Locations of North China Plain (NCP, 32°–40° N, 114°–121° E) and other three major air pollution regions, Beijing-Tianjin-Hebei (BTH, 37°–41° N, 114°–118° E), Yangtze River Delta (YRD, 30°–33° N, 118°–122° E), and Pearl River Delta (PRD, 21.5°–24° N, 112°–115.5° E) in China with terrain heights included and (b) location of ultraviolet (UV) radiation observational site, YCA (Yucheng site), areas covered by the NCP region and mountains surrounded.



750 **Figure 2.** A comparison of spatial distributions of monthly mean of MDA8 O_3 (ppb) (a, b) and $PM_{2.5}$ (μg m^{-3}) (c, d) obtained from in-situ observations, AOD (e, f) and tropospheric column of NO_2 ($TCNO_2$, 10^{16} cm^{-2}) (g, h) derived from satellite observations between 2013 (in left column) and 2019 (in right column) in eastern China (NCP indicated by the box).



755 **Figure 3.** A comparison of spatial distributions of monthly mean of T_{2max} (℃, a and b), wind speed (m s^{-1}, c and d), surface reaching short-wave radiation (W m^{-2}, e and f) and PBLH (m, g and h) between 2013 (in left column) and 2019 (in right column) in eastern China (the NCP indicated by the box).



760 **Figure 4.** Long-term changes in monthly mean of (a) MDA8 O_3, (b) $PM_{2.5}$, (c) AOD, (d) $TCNO_2$, (e) SSA, (f) T_{2max}, and (g) PBLH averaged over the North China Plain in June over the period of 2013–2019.

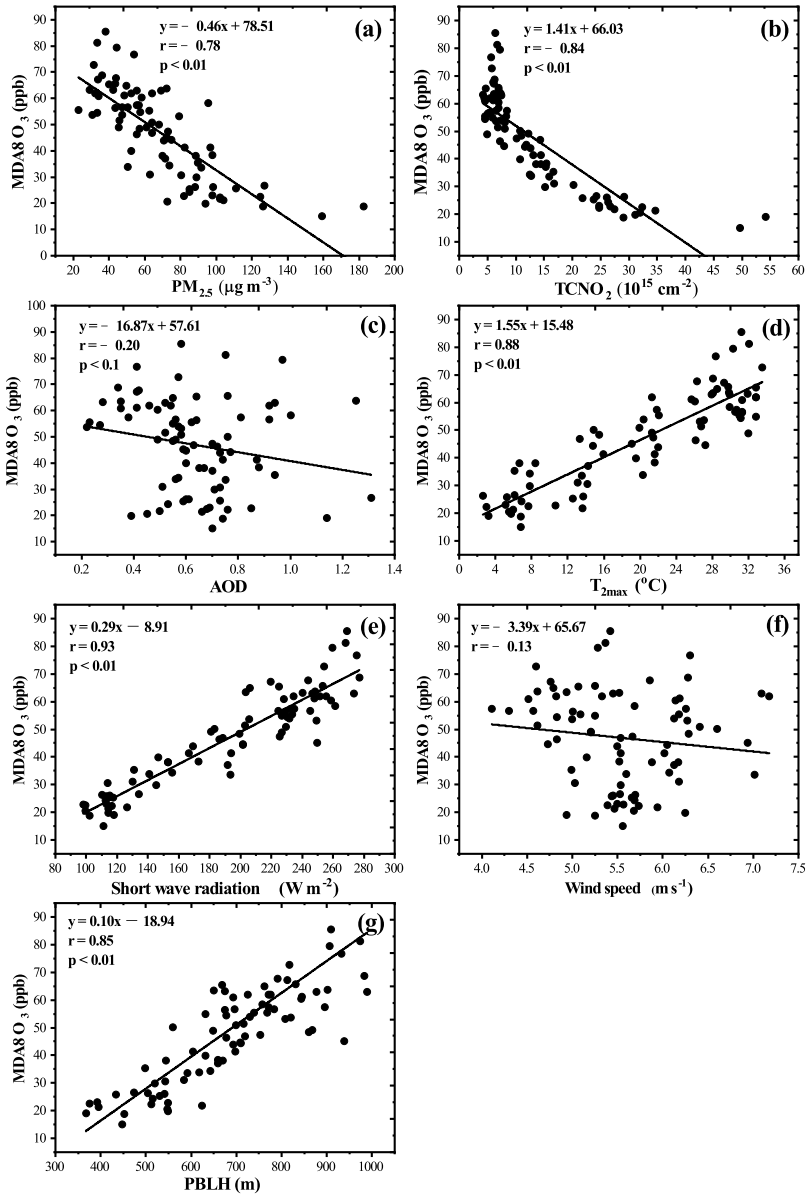


Figure 5. Response of MDA8 O_3 to (a) $PM_{2.5}$, (b) $TCNO_2$, (c) AOD, (d) T_{2max}, (e) shortwave radiation, (f) wind speed, and (g) PBLH observed in the NCP region, China during 2013–2019.

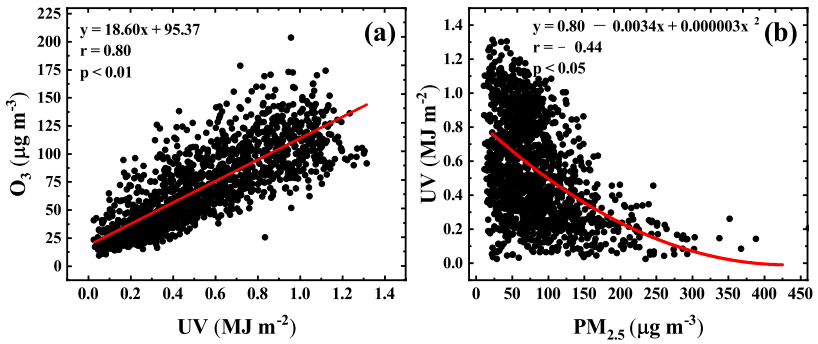


Figure 6. a) The relationships of surface O_3 concentrations (hourly) with (a) UV radiation and (b) UV radiation with $PM_{2.5}$ concentrations based on the observations at Yucheng site during the time period of 08–17 LT in June, 2013–2016.

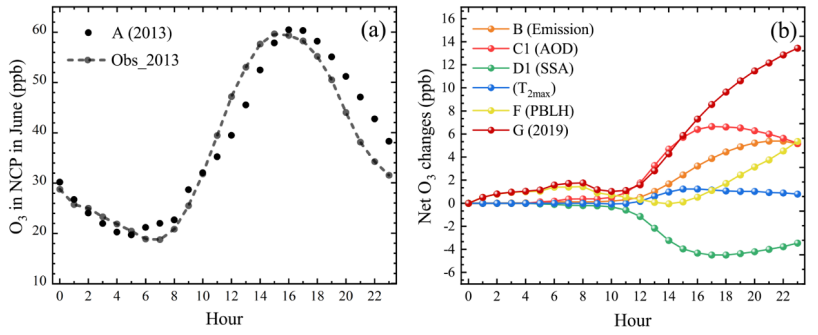


Figure 7. Comparisons of (a) regional averaged surface O_3 observations in NCP and simulated surface O_3 (A, control case) and (b) simulated net changes in O_3 among different driving-factor conditions.

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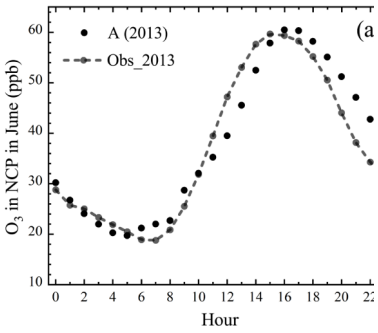

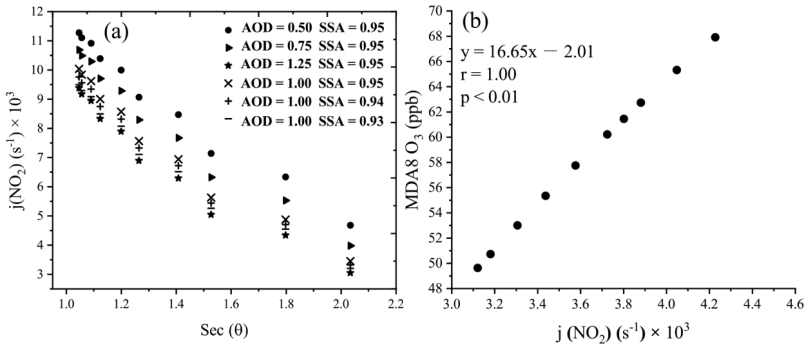

Figure 8. (a) response of photolysis rate of NO_2, $j(NO_2)$ to different values of aerosol optical depth (AOD) and single scatter factor (SSA) and (b) change in MDA8 O_3 with $j(NO_2)$ simulated by the MM model for the cases with SSA=0.95 and AOD varying from 0.5 to 1.25.

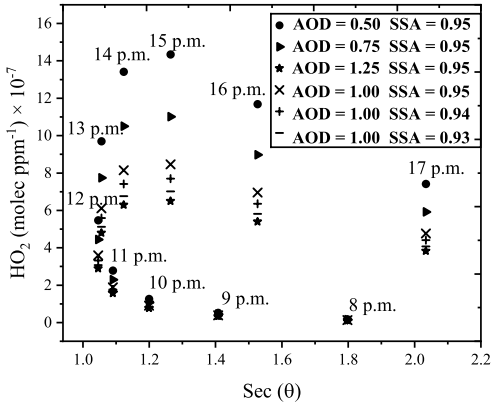

Figure 9. Response of concentrations of HO_2 to different values of aerosol optical depth (AOD) and single scatter factor (SSA).

Supplement of

Rapid increase in summer surface ozone over the North China Plain during 2013–2019: a side effect of particulate matters reduction control?

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List of Supplemental Figures

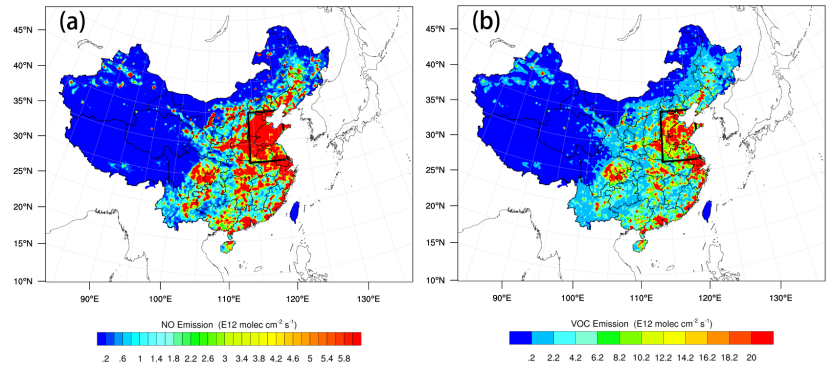

Figure S1. Spatial distributions of a) NO_x and b) VOCs emissions from Multi-resolution Emission Inventory in June for year-2013 in China used in this study (http://www.meicmodel.org/).

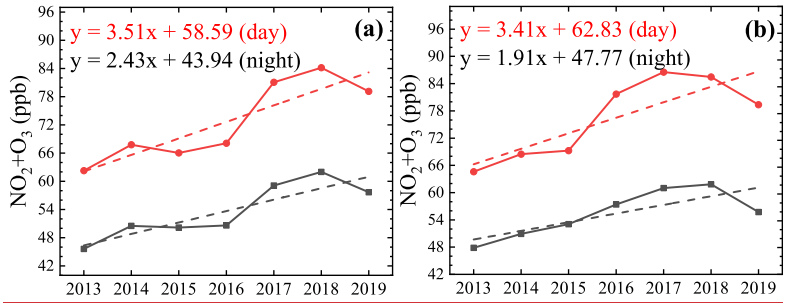

Figure S2. Long-term changes in monthly mean of observed Ox (NO_2 +O_3) averaged over the North China Plain (a) and urban areas Beijing in daytime (redline) and nighttime (blackline) in June over the period of 2013–2019.

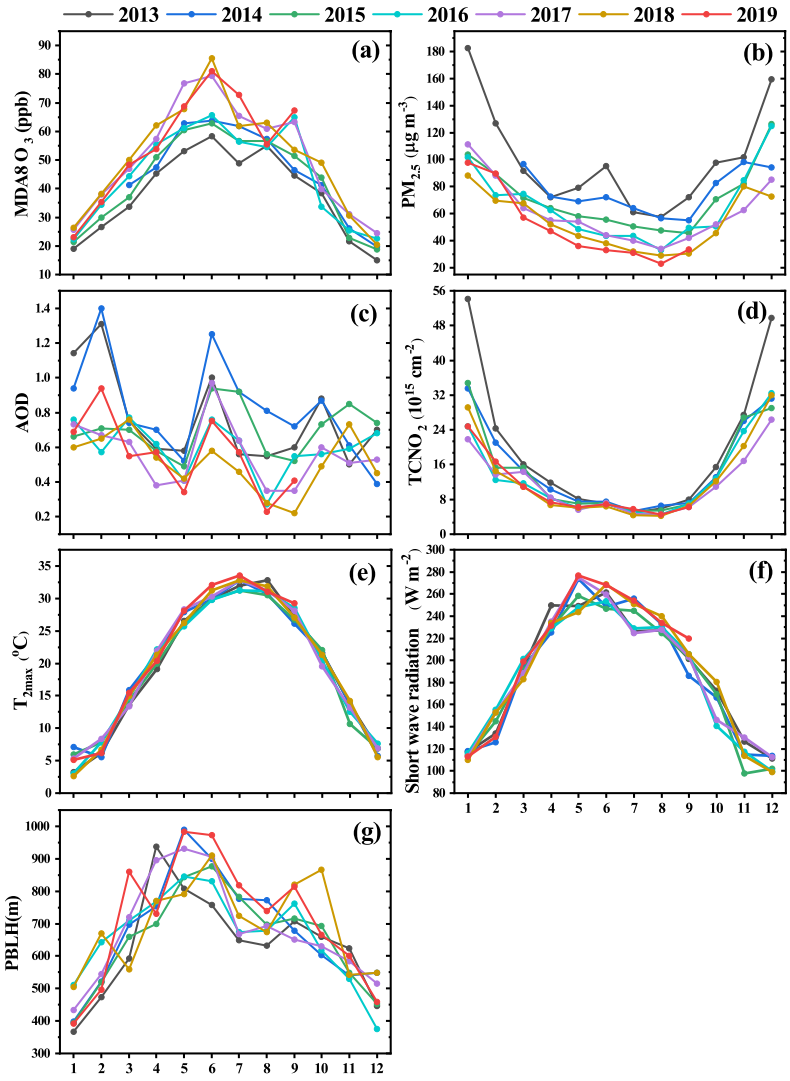

Figure S3. A comparison of monthly means of (a) the maximum daily 8-h average (MDA8) O_3 (ppb), (b) particulate matters with aerodynamic diameter of 2.5 micrometers ($PM_{2.5}$) ($\mu g\ m^3$), (c) aerosol optical depth (AOD), (d) Tropospheric Column of NO_2 ($TCNO_2$) (10^{15} cm^{-2}), (e) daily max temperature at 2 m (T_{2max}) (°C), (f) short-wave radiation (W m^{-2}), and (g) planetary boundary layer height (PBLH) (m) in North China Plain over the period of 2013–2019.

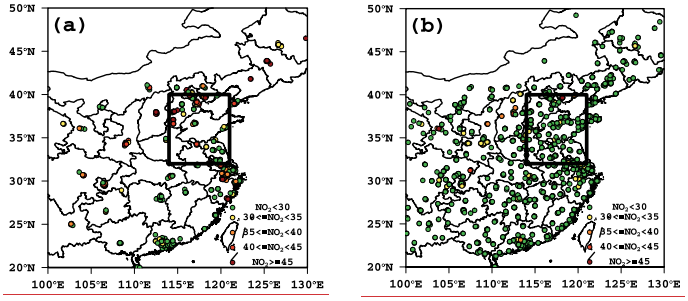

Figure S4. A comparison of spatial distributions of monthly mean of NO_2 (μg m^{-3}) monitored by China National Environmental Monitoring Center between (a) 2013 and (b) 2019 in eastern China (NCP indicated by the box).

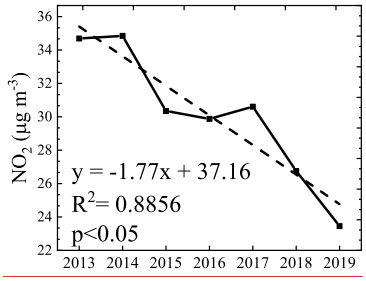

Figure S5. Long-term changes in monthly mean of observed NO_2 averaged over the North China Plain in June over the period of 2013–2019.

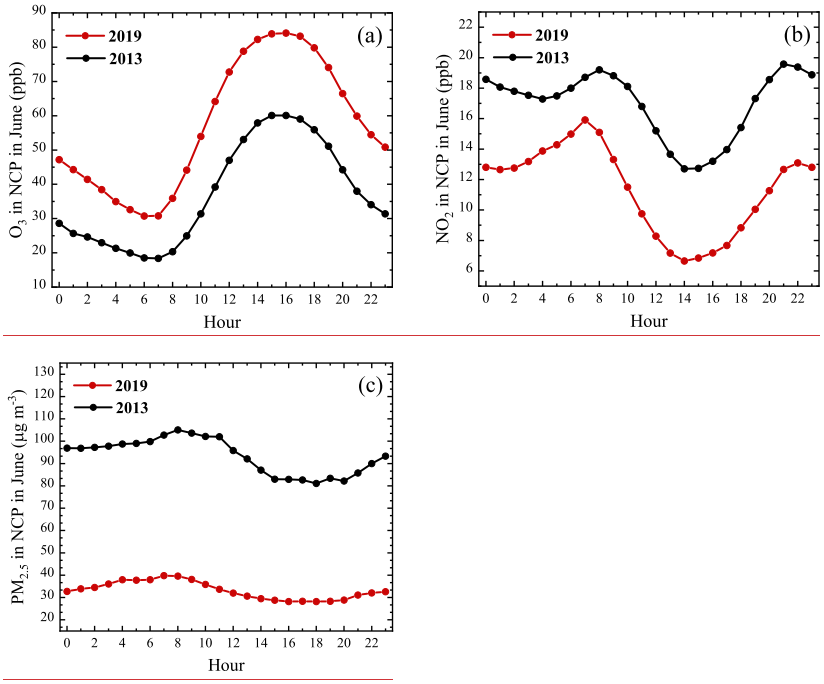

Figure S6. Average diurnal profiles of (a) O_3, (b) NO_2, (c) $PM_{2.5}$ in June of 2013 (black lines) and 2019 (red lines).