Impacts of aerosol direct effects on tropospheric ozone through changes in atmospheric dynamics and photolysis rates

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Abstract. Aerosol direct effects (ADE), i.e., scattering and absorption of incoming solar radiation, reduce radiation reaching the ground and the resultant photolysis attenuation can decrease ozone (O₃) formation in polluted areas. One the other hand, evidence also suggests that ADE associated cooling suppresses atmospheric ventilation thereby enhancing surface-level O₃. Assessment of ADE impacts is thus important for understanding emission reduction strategies that seek co-benefits associated with reductions in both particulate matter and O₃ levels. This study quantifies the impacts of ADE on tropospheric ozone by using a two-way online coupled meteorology and atmospheric chemistry model, WRF-CMAQ, instrumented with process analysis methodology. Two manifestations of ADE impacts on O₃ including changes in atmospheric dynamics (ΔDynamics) and changes in photolysis rates (ΔPhotolysis) were assessed separately through multiple scenario simulations for January and July of 2013 over China. Results suggest that ADE reduced surface daily maxima 1h O₃ (DM1O₃) in China by up to 39 µg m⁻³ through the combination of ΔDynamics and ΔPhotolysis in January, but enhanced surface DM1O₃ by up to 4 µg m⁻³ in July. Increased O₃ in July is largely attributed to ΔDynamics which causes a weaker O₃ sink of dry deposition and a stronger O₃ source of photochemistry due to the stabilization of atmosphere. Meanwhile, surface OH is also enhanced at noon in July, though its daytime average values are reduced in January. An increased OH chain length and a shift towards more VOC-limited condition are found due to ADE in both January and July. This study suggests that reducing ADE may have potential risk of increasing O₃ in winter, but it will benefit the reduction of maxima O₃ in summer.

1. Introduction

Photochemistry in the atmosphere is a well-known source for tropospheric ozone (O₃) (e.g., Haagen-Smit and Fox, 1954) and is determined by ambient levels of O₃ precursors (i.e., NOₓ and VOC) and photolysis rates which are largely influenced by meteorological factors such as solar irradiance and temperature. It is well known that aerosols influence radiation through light
scattering and absorption, thereby modulating atmospheric radiation and temperature. These aerosol direct effects (ADE) can then impact thermal and photochemical reactions leading to formation of O$_3$ (Dickerson et al., 1997). Recent studies suggest that the aerosol induced reduction in solar irradiance leads to lower photolysis rates and less O$_3$ (e.g., Benas et al., 2007), therefore extensive aerosol reductions, particularly in developing regions such as in East Asia, may pose a potential risk by enhancing O$_3$ levels (Bian et al., 2007; Anger et al., 2016; Wang et al., 2016). For example, Wang et al (2016) found that because of ADE, the surface 1h maximum ozone (noted as DM1O$_3$) was reduced by up to 12% in eastern China during the EAST-AIRE campaign, suggesting that benefits of PM$_{2.5}$ reductions may be partially offset by increases in ozone associated with reducing ADE.

Ambient O$_3$ levels are influenced by several sources and sinks. The modulation of photolysis rates by ADE is only one manifestation of ADE impacts on O$_3$. In addition, ADE modulate the temperature (e.g., Hansen et al., 1997; Mitchell et al., 1995), atmospheric ventilation (e.g., Jacobson et al., 2007; Mathur et al., 2010), cloud and rainfall (e.g., Albrecht, 1989; Liou and Ou, 1989; Twomey, 1977) which also influence the O$_3$ concentrations. Therefore, ADE can impact air quality through multiple pathways and process chains (Jacobson, 2002; 2010; Jacobson et al., 2007; Wang et al., 2014; Xing et al., 2015a; Ding et al., 2016). For example, Xing et al (2015a) suggested that the O$_3$ response to ADE is largely contributed by the increased precursor concentrations which enhance the photochemical reaction, presenting an overall positive response of O$_3$ to ADE by up to 2-3% in eastern China. Assessment of separate contribution from individual processes is necessary for fully understanding how ADE impact O$_3$.

In China, atmospheric haze is currently one of the most serious environmental issue of concern. Over the next decade, the national government plans to implement stringent control actions aimed at lowering the PM$_{2.5}$ concentrations (Wang et al., 2017). Speculation on whether such extensive aerosol controls will enhance O$_3$ and oxidation capacity need to be carefully assessed and quantified. Many studies suggest that aerosols may have substantial impacts on ozone through heterogeneous reactions including hydrolysis of N$_2$O$_5$, irreversible absorption of NO$_2$ and NO$_3$, as well as the uptake of HO$_2$ (Tang et al., 2004; Tie et al., 2005; Li et al., 2011; Lou et al., 2014). While our model contains comprehensive treatment of the heterogeneous hydrolysis of N$_2$O$_5$ (Davis et al., 2008; Sarwar et al., 2012; Sarwar et al., 2014), we have not quantified its impacts on ozone in this study. However, ADE impacts on ozone have not been well evaluated previously. Accurate assessment of the multiple ADE impacts is a prerequisite for accurate policy decision. The process analysis (PA) methodology is an advanced probing tool that enables quantitative assessment of integrated rates of key processes and reactions simulated in the atmospheric model (Jang et al, 1995; Zhang et al., 2009; Xu et al., 2008; Liu et al., 2010; Xing et al., 2011). In this study, we apply the PA methodology in the two-way coupled meteorology and atmospheric chemistry model, i.e., Weather Research and Forecast (WRF) model coupled with the Community Multiscale Air Quality (CMAQ) model developed by U.S. Environmental Protection Agency (Pleim et al., 2008; Mathur et al., 2010; Wong et al., 2012; Yu et al., 2013; Mathur et al., 2014; Xing et al.,
to examine the process chain interactions arising from ADE and quantify their impacts on O\textsubscript{3} concentration.

The manuscript is organized as following. A brief description of the model configuration, scenario design and PA method is presented in section 2. The O\textsubscript{3} response to ADE is discussed in section 3.1. PA analyses are discussed in section 3.2-3.3. The summary and conclusion is provided in section 4.

2. Method

2.1 Modeling System

The two-way coupled WRF-CMAQ model has been detailed and fully evaluated in our previous papers (Wang et al., 2014; Xing et al., 2015a, b). The meteorological inputs for WRF simulations were derived from the NCEP FNLFinal) Operational Global Analysis data which has 1 degree spatial and 6-hour temporal resolution. NCEP ADP Operational Global Surface Observations were used for surface reanalysis and four dimensional data assimilation. We have tested and chosen proper strength of nudging coefficients, i.e., 0.00005 sec\textsuperscript{-1} is used for nudging of both u/v-wind and potential temperature, 0.00001 sec\textsuperscript{-1} is used for nudging of water vapor mixing ratio, to improve model performance without dampening the effects of radiative feedbacks (Hogrefe et al., 2015; Xing et al., 2015b). In the model version used here, concentrations of gaseous species and primary and secondary aerosols are simulated by using Carbon Bond 05 gas-phase chemistry (Sarwar et al., 2008) and the sixth-generation CMAQ modal aerosol model (AERO6) (Appel et al., 2013). The aerosol optical properties were estimated by the coated-sphere module (i.e., BHCOAT, Bohren and Huffman, 1983) based on simulated aerosol composition and size distribution (Gan et al., 2015). In the coupled model, the estimated aerosol optical properties are fed to the RRTMG radiation module in WRF, thus updating the simulated atmospheric dynamics which then impact the simulated temperature, photolysis rate, transport, dispersion, deposition and cloud mixing and removal of pollutants. Due to large uncertainties associated with the representation of aerosol impacts on cloud droplet number and optical thickness, the indirect radiative effects of aerosols are not included in the current calculation.

The gridded emission inventory, initial and boundary conditions are consistent with our previous studies (Zhao et al., 2013a, b; Wang et al., 2014), while the simulated domain is extended slightly to cover the entire China, as shown in Figure 1. A better model performance in the simulation of dynamic fields including total solar radiation, PBL height data as well as PM\textsubscript{2.5} concentrations were suggested after the inclusion of ADE (Wang et al., 2014). In this study, the model performance in the simulation of O\textsubscript{3} will be evaluated through the comparison with observations from 74 cities across China from the China National Urban Air Quality Real-time Publishing Platform (http://113.108.142.147:20035/emcpublish/). The simulation period is selected as January 1\textsuperscript{st} to 31\textsuperscript{st} and July 1\textsuperscript{st} to 31\textsuperscript{st} in 2013 to represent winter and summer conditions, respectively. Five regions are selected for analysis, including Jing-Jin-Ji area (denoted JJJ), Yangzi-River-Delta (denoted YRD), Perl-River-Delta (denoted PRD), Sichuan Basin (denoted SCH) and Hubei-Hunan area (denoted HUZ), as shown in Figure 1.
2.2 Simulation Design

Table 1 summarizes the scenario design in this study. In the baseline simulation (denoted SimBL), no aerosol feedbacks either on photolysis rates or radiations was taken into account. In simulation SimNF, only aerosol feedbacks on photolysis rates were considered by embedding an inline photolysis calculation in the model which accounted for modulation of photolysis due to ADE. Finally, in simulation SimSF aerosol feedbacks were considered on both photolysis rates and radiation calculations. Differences between the simulations of SimNF and SimBL are considered as ADE impacts on O$_3$ through photolysis (denoted $\Delta$Photolysis). Similarly, differences between the simulations of SimSF and SimNF are considered as the ADE impacts on O$_3$ through dynamics (denoted $\Delta$Dynamics), and differences between the simulations of SimSF and SimBL represents as the combined ADE impacts on O$_3$ due to both photolysis and dynamics (denoted $\Delta$Total).

2.3 Process Analysis

In this study the PA methodology is used in the WRF-CMAQ model to analyze processes impacting simulated O$_3$ level. The Integrated Process Rates (IPRs) track hourly contributions to O$_3$ from seven major modeled atmospheric processes that act as sinks or sources of O$_3$. These processes are gas phase chemistry (denoted CHEM), cloud processes (i.e., the net effect of aqueous-phase chemistry, below- and in-cloud scavenging, and wet deposition, denoted CLDS), dry deposition (denoted DDEP), horizontal advection (denoted HADV), horizontal diffusion (denoted HDIF), vertical advection (denoted ZADV), and turbulent mixing (denoted VDIF). The difference in IPRs among SimBL, SimNF and SimSF represents the response of individual process to ADE. To enable the consistent examination of changes in the process due the ADE across all concentration ranges, we examine changes in the IPRs normalized by the O$_3$ concentrations. The differences in these process rates (expressed in units of hr$^{-1}$) between the SimBL, SimSF, SimNF then provide estimates of the changes in process rates resulting from ADE and are shown in the 2nd-4th columns of Figure 4, and (b)-(d) of Figure 5 and 6.

Integrated Reaction Rates (IRR$s$) are used to investigate the relative importance of various gas-phase reactions in O$_3$ formation. Following the grouping approach of previous studies (Zhang et al., 2009; Liu et al., 2010; Xing et al., 2011), the chemical production of total odd oxygen (O$_x$) and the chain length of hydroxyl radical (OH) are calculated. Additionally, the ratio of the chemical production rate of H$_2$O$_2$ to that of HNO$_3$ ($P_{H2O2}/P_{HNO3}$) is an estimated indicator of NO$_x$- or VOC- limited conditions for O$_3$ chemistry.

3. Results

3.1 O$_3$ response to ADE

The simulated surface DM1O$_3$ in SimBL, SimNF and SimSF are compared in Figure 2a-c. In January, higher DM1O$_3$ concentrations are seen in PRD where solar radiation is stronger than in the north. The model generally captured the spatial
pattern with highest DM1O3 in PRD over the simulated domain. Simulated DM1O3 in YRD, SCH and HUZ are higher than observations. Such overestimation might be associated with the relative coarse spatial resolution in the model. NO titration effects in urban areas were not well represented in the model. In July, high DM1O3 areas are located towards the north, especially in the JJJ and YRD regions which have relatively larger NOx and VOC emission density and favorable meteorological condition (e.g., less rain and moderate solar radiation).

In January, O3 production in north China is occurring in a VOC-limited regime (e.g., Liu et al., 2010), thus increases in NOx at the surface stemming from the stabilized atmosphere by ADE (Jacobson et al., 2007; Mathur et al., 2010; Ding et al., 2013; Xing et al., 2015) inhibit O3 formation due to enhanced titration by NO. As seen in Figure 2d, the ΔDynamics reduced DM1O3 in eastern China by up to 24 μg m⁻³, but slightly increased DM1O3 in parts of southern China by up to 7 μg m⁻³. The decrease in incoming solar radiation due to ADE significantly reduces the photolysis rates in east China. As seen in Figure 2e, the ΔPhotolysis reduced DM1O3 domain-wide by up to 16 μg m⁻³. The combined effect of both ΔDynamics and ΔPhotolysis, results in an overall reduction in DM1O3 as evident across the JJJ and SCH regions with monthly-average reductions up to 39 μg m⁻³.

In July, the O3 chemistry changes from a VOC-limited to a NOx-limited regime across most of China. Therefore, increase in NOx concentration due to the stabilization of atmosphere associated with the ADE, facilitates O3 formation. The ΔDynamics increased DM1O3 across most areas of China, particularly in JJJ, YRD and SCH by up to 5 μg m⁻³, with the exception of the PRD region where DM1O3 decreased. The ΔPhotolysis results in contrasting impacts in July compared to January, as it increased DM1O3 in most polluted areas including JJJ, YRD, PRD, HUZ, although the solar radiances were reduced due to ΔPhotolysis. This behavior is likely due to enhanced aerosol scattering associated with higher summer-time SO2² levels during summer (He and Carmichael, 1999; Jacobson, 1998). Similar results were found in Tie et al (2005) who reported that surface-layer photolysis rates in eastern China were reduced less significantly in summer than in winter. The resultant enhancements in photolysis rates can then cause the noted higher concentrations. More importantly, the diurnal analysis (discussed in the next section) suggested that the reduced photolysis during the early morning in SimNF, enhances the ambient precursor concentrations (due to less reaction in early morning) at noon when O3 reaches the daily maximum. This increase in precursor concentrations then leads to enhanced O3 formation later in the day which compensates for or even overwhelms the disbenefit from the reduced solar radiances. In summer, ΔDynamics results in a much stronger influence on DM1O3 than ΔPhotolysis, and the combined impact of ADE increased O3 in most of regions in China by up to 4 μg m⁻³.

The impact of the ADE on O3 is further explored by examining the relationship between the observed and simulated O3 concentrations (DM1O3, daily values of the cities located in China) as a function of the observed PM2.5 concentrations (observed daily averaged values in those cities), as displayed in Figure 3. The predicted ozone concentrations under both low- and high- PM2.5 levels are compared in Table 2. In regards to model performance for DM1O3 simulations, the model generally
exhibits a slight high bias in January but a low bias in July across the 5 regions. The inclusion of ADE moderately reduced O$_3$ concentrations in January and slightly increased O$_3$ in July, resulting in reduction in bias and improved performance for DM1O$_3$ simulation in both January and July for most of regions. Comparing the O$_3$ responses to ADE (see ∆-ADE in Table 2) under low- and high- PM$_{2.5}$ levels, reveals that O$_3$ responses to ADE are larger under high PM$_{2.5}$ levels, indicating the positive correlations between O$_3$ responses and PM$_{2.5}$ levels.

Interestingly, from low to moderate PM$_{2.5}$ levels (i.e., PM$_{2.5} < 120$ µg m$^{-3}$), higher O$_3$ concentration occur with higher PM$_{2.5}$ concentrations, which is evident in both observations and simulations, suggestive of common precursors (e.g., NO$_3$), source sectors, and/or transport pathways contributing to both O$_3$ and PM$_{2.5}$ in these regions. However, a negative correlation between O$_3$ and PM$_{2.5}$ is evident in winter when the PM$_{2.5}$ can reach high levels larger than 120 µg m$^{-3}$, indicating the strong ADE impacts on O$_3$ through both feedbacks to dynamics and photolysis which significantly reduced O$_3$.

### 3.2 IPRs response to ADE

To further explore the ADE impacts on simulated O$_3$, the integrated process contributions are further analyzed in three ways: (a) 24-hour diurnal variations of process contributions to simulated surface O$_3$ (Figure 4), (b) vertical profiles from ground up to 1357 m AGL (above ground level, in model layer 1-10) at noon (Figure 5), and (c) correlations with near-ground PM$_{2.5}$ (average concentrations between the ground and 355m AGL, model layer 1-5) (Figure 6). In the following, we limit our discussion to analysis of model results for the JJJ region which exhibited the strongest ADE among the regions; similar results were found for the other 4 regions and can be found in the Supporting Information section.

Diurnal variation of process contributions from chemistry (CHEM), dry deposition (DDEP) and vertical turbulent mixing (VDIF) which together contribute to more than 90% of the O$_3$ rate of change for the JJJ region, are illustrated in Figure 4. The diurnal variation of IPRs for other processes and their response to ADE are displayed in Figure S1 for JJJ and Figure S2-S5 for other 4 regions.

For surface-level O$_3$, VDIF is the major source and DDEP is the major sink (Figure S1). The stabilization of atmosphere due to ∆Dynamics leads to lower dry deposition rates (due to lower dry deposition velocity from the enhanced aerodynamic resistance) and thus increases surface O$_3$. The largest impact of ∆Dynamics on DDEP occurs during early morning and late afternoon which is consistent with the response of the PBL height to ADE noted in our previous analysis (Xing et al., 2015). Expectedly, CHEM is the second largest sink for surface O$_3$ during January, but a source for surface O$_3$ during the daytime in July. The ∆Dynamics increased the surface O$_3$ around noon in both January and July for almost all regions (no impacts in PRD and YRD in January, see Figure S2-S3), since increased stability due to ∆Dynamics concentrated more precursors locally, leading to enhanced O$_3$ formation during the photochemically most active period of the day. The ∆Dynamics reduced the surface O$_3$ around late afternoon in January at all regions. This is because the increased atmospheric stability during late
afternoon and evening hours increased NO₃ concentration which titrated more O₃. The ΔPhotolysis reduced surface O₃ in all regions in January. These reductions were more pronounced during the early morning hours when the photolysis rate are most sensitive to the radiation intensity. The ΔPhotolysis resulted in comparatively larger reductions in surface O₃ during the early morning and late afternoon hours in July, but slightly increased surface O₃ at noon for most of the regions. This increase in O₃ can be hypothesized to result from the following sequence of events. Slower photochemical reaction in the morning in the ΔPhotolysis case lead to higher levels of precursors, whose accumulation then enhances O₃ formation at noon. This hypothesis is further confirmed by the changes in the diurnal variation of NO₂ which suggest that higher NO to NO₂ conversion during early morning results in enhanced daytime NO₂ levels (see Figure S6), consequently leading to higher noon-time O₃.

For aloft O₃ (from 100 to 1600 meters above ground) as seen in Figure 5, CHEM is the major source for O₃ at noon both in January and in July. The ΔDynamics increased near-surface O₃ (below 500m, model layer 1-6), but reduced upper-level O₃ (above 500m, model layer 7-10), because increased stability of the atmosphere concentrated precursors emissions within a shallower layer resulting in higher O₃ production. The ΔPhotolysis case considerably reduced near-surface O₃ at noon in January. In July, ΔPhotolysis increased upper-level O₃ at noon. Higher levels of precursors at noon might be the reason for such enhancement (see Figure S6).

The daytime near-ground-averaged (between the ground and 350m AGL, layers 1-5) IPR responses to ADE are shown in Figure 6 for JJJ and in Figure S7 for other regions. The IPR and its responses are presented as a function of near-ground-averaged PM₂.₅ concentrations. As shown in Figure 6, as PM₂.₅ concentrations increase, the positive contribution of CHEM in July become larger while the negative contribution of CHEM in January become smaller. The overall ADE enhanced CHEM and thus increased O₃ concentration in July, and such enhancement are generally larger for higher PM₂.₅ loading. In contrast, in January overall ADE resulted in higher rates of O₃ destruction due to chemistry (negative contribution of CHEM), and the magnitude of this sink increased as PM₂.₅ concentrations increase. The reduction of O₃ stemming from the enhancements in the chemical sinks is the dominant impact of ADE in January. The enhanced positive contribution of CHEM due to ΔDynamics was partially compensated by the reduction from ΔPhotolysis (see Figure S7), resulting in a slight increase in the positive CHEM contribution to O₃ in July.

DDEP is the major sink of daytime O₃ during both January and July. The increased stability due to ADE reduced deposition velocity and thus increases O₃. These effects become larger with increasing PM₂.₅ concentrations. Thus, weaker removal of O₃ from DDEP associated with ADE, contributed to higher O₃ in most regions during both January and July. Enhanced O₃ source of CHEM and reduced O₃ sink of DDEP is the dominant impact of ADE in July.

3.3 IRR response to ADE

The simulated mid-day average (11:00-13:00 local time) surface O₃ (defined as the sum of O, O₃, NO₂, NO₃, N₂O₅, HNO₃, PNA, NTR, PAN and PANX) and OH and their responses to ADE are shown in Figure 7. Both O₃ and OH are significantly
reduced in the ΔPhotolysis case in January throughout the modeling domain. Both O₃ and OH also show reductions in the middle portions of east China in the ΔDynamics case in January. Together, the combined ADE impacts result in reduced O₃ and OH in January, with widespread reductions primarily due to ADE on photolysis. In July, ΔPhotolysis increased mid-day OH across most of China (Figure 7) which is consistent with the increase of O₃ at noon stemming from a higher level of precursors accumulation due to ΔPhotolysis. The overall ADE impact on OH is controlled by ΔPhotolysis, and result in increased mid-day OH across most of China. For O₃, however, the impact of ΔDynamics overwhelms the impact from ΔPhotolysis, resulting in increase in O₃ concentrations in east China including YRD, SCH and HUZ.

To further examine the response of O₃ to ADE, in Figure 8 we examine vertical profiles of the integrated reaction rates at noon for the JJJ region. The stabilization of the atmosphere due to ΔDynamics concentrates precursors within a lower PBL, resulting in an increased total O₃ production rate (P_{totalO3}) mostly in near-ground model layers (below 500m, model layer 1-6); in magnitude aloft (above 500m, model layer 7-10), this change in P_{totalO3} is smaller in January, and become decreasing in July. The reduction of P_{totalO3} due to ΔPhotolysis is greatest at the surface in January, and declines with altitude, and even becomes reversed at high layers (about 1300m, model layer 10) (Figure 8a). The overall ADE impact in January is mainly dominated by ΔPhotolysis which largely overwhelms the impact of ΔDynamics (Figure 8a). However, in July, ΔPhotolysis enhanced P_{totalO3} across all layers. The P_{totalO3} shows small decreases at high altitudes but significant increase in near-ground model layers (below 500m, model layer 1-6) due to the combined ADE in July.

The changes in vertical profiles of production rates of new OH (P_{NewOH}) and reacted OH (P_{ReactedOH}) are similar to those of P_{totalO3}, with the noted decreases in January dominated by ΔPhotolysis. In contrast, the increases in July result from contribution from both ΔPhotolysis and ΔDynamics.

Analysis of the chain length is important to understand the characteristics of chain reaction mechanisms. The OH chain length (denoted OH_CL) is determined by the ratio of P_{ReactedOH} to P_{NewOH}. ΔDynamics concentrated more NOₓ at surface, thus leading to an increased OH_CL (i.e., more reacted OH than new OH) in the near-ground layers, but a decreased OH_CL in the upper layers. In January, the ΔPhotolysis reduced P_{NewOH} more than P_{ReactedOH} (probably because of more abundance of NOₓ resulting from photolysis attenuation and consequently reduced photochemistry), thereby leading to an increased OH_CL. In July, ΔPhotolysis enhanced both P_{NewOH} and P_{ReactedOH}, particularly in the upper layers. The OH_CL is increased by ΔPhotolysis because higher NOₓ levels (see Figure S6) cause more reacted OH to be reacted. Thus the surface OH_CL at noon is increased in both January and July from combined ADE of ΔPhotolysis and ΔDynamics, indicating a stronger propagation efficiency of the chain.

The production rates of H₂O₂ (P_{H2O2}) and HNO₃ (P_{HNO3}) and their responses to ADE are also summarized in Figure 8 (average for mid-day hours) for the JJJ region (similar illustrations for the other regions can be found in the supplemental Figures S8-S11. Smaller ratios of P_{H2O2}/P_{HNO3} are noted in January compared to July, indicating a stronger VOC-limited regime in January
for all regions. The ∆Dynamics increases \( P_{\text{HNO}_3} \) but decreases \( P_{\text{H}_2\text{O}_2} \) in both January and July because the enhanced NO\(_x\) at the surface in a more stable atmosphere likely shifts O\(_3\) chemistry towards NO\(_x\)-rich condition. The ∆Photolysis reduced both \( P_{\text{H}_2\text{O}_2} \) and \( P_{\text{HNO}_3} \) but the ratio of \( P_{\text{H}_2\text{O}_2}/P_{\text{HNO}_3} \) is decreased due to larger reduction in \( P_{\text{H}_2\text{O}_2} \) than \( P_{\text{HNO}_3} \). The combined impacts of ∆Dynamics and ∆Photolysis result in a shift towards more VOC-limited conditions in the near-surface layers during both January and July.

4. Summary

The impacts of ADE on tropospheric ozone were quantified by using the two-way coupled meteorology and atmospheric chemistry WRF-CMAQ model instrumented with the process analysis methodology. Two manifestations of ADE impacts on O\(_3\), changes in atmospheric dynamics (∆Dynamics) and changes in photolysis rates (∆Photolysis), were systematically evaluated through simulations that isolated their impacts on modeled process rates over China for winter and summer conditions (represented by the months of January and July in 2013, respectively). Results suggest that the model performance for surface DM1O\(_3\) simulations improved after the inclusion of ADE which moderately reduced the high-bias in January and low-bias in July. In winter, the inclusion of ADE impacts resulted in an overall reduction in surface DM1O\(_3\) across China by up to 39 µg m\(^{-3}\). Changes both in photolysis and atmospheric dynamics due to ADE contributed to the reductions in DM1O\(_3\) in winter. In contrast during July, the impact of ADE increased surface DM1O\(_3\) across China by up to 4 µg m\(^{-3}\). The summertime increase in DM1O\(_3\) results primarily from ADE induced effects on atmospheric dynamics. It can thus be postulated that reducing ADE will have potential risk of increasing O\(_3\) in winter, but will benefit the reduction of maximum O\(_3\) in summer.

Results from IPR analysis suggest that the ADE impacts exhibit strong vertical and diurnal variations. The ADE induced decrease in modeled DM1O\(_3\) in January primarily results from ∆Photolysis which reduced the chemical production of O\(_3\) in the near-ground layers. The increase in DM1O\(_3\) in July due to ADE results from a weaker dry deposition sink as well as a stronger chemical source due to higher precursor concentrations in a more stable and shallow PBL. These impacts become stronger under higher PM\(_{2.5}\) concentrations when ADE are larger.

The combined ADE impacts reduce O\(_3\) in January due to ∆Photolysis, but slightly increase O\(_3\) in July due to ∆Dynamics. OH is reduced by ADE in January. However, mid-day OH concentrations during summertime show enhancements associated with both ∆Photolysis and ∆Dynamics, indicating a stronger mid-day atmospheric oxidizing capacity in July. An increased OH chain length in the near-ground layers is modeled both in January and July, indicating a stronger propagation efficiency of the chain reaction. In both January and July, \( P_{\text{HNO}_3} \) is increased and \( P_{\text{H}_2\text{O}_2} \) is decreased due to ∆Dynamics, and both are reduced due to ∆Photolysis. The ratio of \( P_{\text{H}_2\text{O}_2}/P_{\text{HNO}_3} \) is decreased due to the combined impacts of ∆Dynamics and ∆Photolysis, indicating a shift towards more VOC-limited conditions due to ADE in the near-ground layers during both January and July.
Thus aerosol direct effects on both photolysis rates as well as atmospheric dynamics can impact \( O_3 \) formation rates and its local and regional distributions. Comparisons of integrated process rates suggest that the decrease in DM1O\(_3\) in January results from a larger net chemical sink due to \( \Delta \)Photolysis, while the increase in DM1O\(_3\) in July is mostly associated with the slower removal due to reduced deposition velocity as well as a stronger photochemistry due to \( \Delta \)Dynamics. The IRR analyses confirm that the process contributions from chemistry to DM1O\(_3\) can be influenced by both \( \Delta \)Dynamics and \( \Delta \)Photolysis. Reduced ventilation associated with \( \Delta \)Dynamics enhances the precursor levels, which increase chemical production rate of \( O_x \) and OH, resulting in greater \( O_3 \) chemical formation at noon during both January and July. One the other hand, reduced photolysis rates in \( \Delta \)Photolysis results in lower \( O_3 \) in January. However, in July lower photolysis rates result in accumulation of precursors during the morning hours which eventually lead to higher \( O_3 \) production at noon.

The comparison of integrated reaction rates from the various simulations also suggest that the increased OH_CL and the shift towards more VOC-limited conditions are mostly associated with the higher NO\(_2\) levels due to ADE. This further emphasizes the importance of NO\(_x\) controls in air pollution mitigation. Traditionally, the co-benefits from NO\(_x\) control for ozone and PM reduction are mostly because that NO\(_x\) is a common precursor for both \( O_3 \) and PM\(_{2.5}\). This study suggests that effective controls on NO\(_x\) will not only gain direct benefits for \( O_3 \) reduction, but also can indirectly reduce peak \( O_3 \) through weakening the ADE from the reduced PM\(_{2.5}\), highlighting co-benefits from NO\(_x\) controls for achieving both \( O_3 \) and PM\(_{2.5}\) reductions.

Reducing aerosols will have substantial impacts on ozone. Quantification of the aerosol influence on ozone is important to understand co-benefits associated with reductions in both particulate matter and ozone. This study focused on the evaluation of ADE impacts which were not well quantified previously. However, the heterogeneous reactions associated with aerosols, as well as the impacts of emission controls of gaseous precursors on both aerosols and ozone also need to be studied in order to fully understand the influence from reducing aerosols on ambient ozone.

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### Table 1: Description of sensitivity simulations in this study

<table>
<thead>
<tr>
<th>Short name</th>
<th>Simulation description</th>
<th>Aerosol impacts on photolysis calculations</th>
<th>Aerosol impacts on radiation calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SimBL</td>
<td>Baseline simulation</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>SimNF</td>
<td>No aerosol feedback simulation</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>SimSF</td>
<td>Aerosol feedback simulation</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### Table 2: Comparison of model performance in ozone prediction across three simulations (monthly average of daily 1h maxima)

<table>
<thead>
<tr>
<th>Region</th>
<th>OBS Low PM$_{2.5}$ (&lt;60µg m$^{-3}$)</th>
<th>Normalized Mean Bias</th>
<th>Δ-ADE* (µg m$^{-3}$)</th>
<th>OBS High PM$_{2.5}$ (&gt;60µg m$^{-3}$)</th>
<th>Normalized Mean Bias</th>
<th>Δ-ADE (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SimSF</td>
<td>SimNF</td>
<td>SimBL</td>
<td>SimSF</td>
<td>SimNF</td>
<td>SimBL</td>
</tr>
<tr>
<td>January</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JJJ</td>
<td>62.52</td>
<td>3%</td>
<td>4%</td>
<td>5%</td>
<td>-1.05</td>
<td>37.02</td>
</tr>
<tr>
<td>YRD</td>
<td>63.89</td>
<td>38%</td>
<td>41%</td>
<td>43%</td>
<td>-2.76</td>
<td>66.74</td>
</tr>
<tr>
<td>PRD</td>
<td>97.25</td>
<td>25%</td>
<td>26%</td>
<td>29%</td>
<td>-4.52</td>
<td>122.61</td>
</tr>
<tr>
<td>HUZ</td>
<td>47.67</td>
<td>172%</td>
<td>173%</td>
<td>193%</td>
<td>-10.17</td>
<td>67.29</td>
</tr>
<tr>
<td>SCH</td>
<td>88.63</td>
<td>-43%</td>
<td>-40%</td>
<td>-38%</td>
<td>-3.85</td>
<td>111.19</td>
</tr>
<tr>
<td>China</td>
<td>76.61</td>
<td>30%</td>
<td>31%</td>
<td>34%</td>
<td>-2.96</td>
<td>62.68</td>
</tr>
<tr>
<td>July</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JJJ</td>
<td>159.27</td>
<td>-29%</td>
<td>-28%</td>
<td>-28%</td>
<td>-0.51</td>
<td>178.54</td>
</tr>
<tr>
<td>YRD</td>
<td>171.04</td>
<td>-31%</td>
<td>-31%</td>
<td>-32%</td>
<td>0.84</td>
<td>233.13</td>
</tr>
<tr>
<td>PRD</td>
<td>129.02</td>
<td>-20%</td>
<td>-19%</td>
<td>-20%</td>
<td>-0.09</td>
<td>312.21</td>
</tr>
<tr>
<td>HUZ</td>
<td>187.44</td>
<td>-36%</td>
<td>-37%</td>
<td>-37%</td>
<td>1.39</td>
<td>208.99</td>
</tr>
<tr>
<td>SCH</td>
<td>163.81</td>
<td>-38%</td>
<td>-38%</td>
<td>-39%</td>
<td>0.77</td>
<td>191.19</td>
</tr>
<tr>
<td>China</td>
<td>145.24</td>
<td>-28%</td>
<td>-28%</td>
<td>-28%</td>
<td>0.3</td>
<td>181.65</td>
</tr>
</tbody>
</table>

*Δ-ADE represents the O$_3$ response to ADE which is calculated from the difference between SimSF and SimBL.
Figure 1: Simulation domain and locations of 5 selected regions in China. Note: JJJ=Jing-Jin-Ji area, YRD=Yangzi-River-Delta area, PRD=Perl-River-Delta area, SCH=Sichuan Basin area, HUZ=Hubei-Hunan area.
<table>
<thead>
<tr>
<th>(a) SimSF</th>
<th>(b) Obs</th>
<th>(c) Sim</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="January_SimSF.png" alt="Image" /></td>
<td><img src="January_Obs.png" alt="Image" /></td>
<td><img src="January_Sim.png" alt="Image" /></td>
</tr>
<tr>
<td>July</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="July_SimSF.png" alt="Image" /></td>
<td><img src="July_Obs.png" alt="Image" /></td>
<td><img src="July_Sim.png" alt="Image" /></td>
</tr>
</tbody>
</table>

(d) ΔDynamic (SimSF – SimNF)  
(c) ΔPhotolysis (SimNF – SimBL)  
(f) ΔTotal (SimSF – SimBL)

January  
| ![Image](January_Dynamic.png) | ![Image](January_Photolysis.png) | ![Image](January_Total.png) |

July  
| ![Image](July_Dynamic.png) | ![Image](July_Photolysis.png) | ![Image](July_Total.png) |

**Figure 2**: Observed and simulated O\(_3\) and its response to ADE (monthly average of daily 1h maxima, \(\mu g\ m^{-3}\))
Figure 3: Observed and simulated surface O₃ concentration against PM₂.₅ concentration (O₃ is daily 1h maxima of monitor sites over China, unit: μg m⁻³; PM₂.₅ is the daily average of those site, unit: μg m⁻³)
Figure 4: Diurnal variation of selected integrated process contributions to surface O$_3$ concentration in JJJ (The calculation is based on the average of grid cells in JJJ; a. Baseline is the simulated O$_3$ in SimBL, unit: ppb hr$^{-1}$; b. $\Delta$-ADE is the difference in normalized IPRs between simulations, unit: hr$^{-1}$; delta_Dynamic is the difference between SimSF and SimNF, delta_Photolysis is the difference between SimNF and SimBL, delta_Total is the difference between SimSF and SimBL.)
<table>
<thead>
<tr>
<th></th>
<th>(a) Baseline</th>
<th>(b) ΔDynamic</th>
<th>(c) ΔPhotolysis</th>
<th>(d) ΔTotal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>January</strong></td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
<td><img src="image3" alt="Graph" /></td>
<td><img src="image4" alt="Graph" /></td>
</tr>
<tr>
<td><strong>July</strong></td>
<td><img src="image5" alt="Graph" /></td>
<td><img src="image6" alt="Graph" /></td>
<td><img src="image7" alt="Graph" /></td>
<td><img src="image8" alt="Graph" /></td>
</tr>
</tbody>
</table>

Figure 5: Vertical profile of integrated process contributions to surface $O_3$ concentration at noon in JJJ (full-layer heights above ground are 40, 96, 160, 241, 355, 503, 688, 884, 1100, 1357 m; a. Baseline is the simulated $O_3$ in SimBL, unit: ppb hr$^{-1}$; b. ΔDynamic is the difference in normalized IPRs between SimSF and SimNF, unit: hr$^{-1}$; c. ΔPhotolysis is the difference in normalized IPRs between SimNF and SimBL, unit: hr$^{-1}$; d. ΔTotal is the difference in normalized IPRs between SimSF and SimBL, unit: hr$^{-1}$)
Figure 6: Integrated process contributions to daytime near-ground-level O₃ under different PM₂.₅ level in JJJ (between the ground and 350m AGL, model layer 1-5)
Figure 7: Impacts of ADE on surface $O_x$ and OH (monthly average of noon time 11am-1pm local time)
<table>
<thead>
<tr>
<th></th>
<th>$P_{\text{totalOx}}$</th>
<th>$\text{OH}_2\text{CL}$</th>
<th>$P_{\text{NewOH}}$</th>
<th>$P_{\text{ReactedOH}}$</th>
<th>$P_{\text{H}_2\text{O}<em>2}/P</em>{\text{HNO}_3}$</th>
<th>$P_{\text{H}_2\text{O}_2}$</th>
<th>$P_{\text{HNO}_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td><img src="chart.png" alt="Baseline chart" /></td>
<td><img src="chart.png" alt="Baseline chart" /></td>
<td><img src="chart.png" alt="Baseline chart" /></td>
<td><img src="chart.png" alt="Baseline chart" /></td>
<td><img src="chart.png" alt="Baseline chart" /></td>
<td><img src="chart.png" alt="Baseline chart" /></td>
<td><img src="chart.png" alt="Baseline chart" /></td>
</tr>
<tr>
<td>$\Delta$Dynamic</td>
<td><img src="chart.png" alt="Dynamic chart" /></td>
<td><img src="chart.png" alt="Dynamic chart" /></td>
<td><img src="chart.png" alt="Dynamic chart" /></td>
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<td><img src="chart.png" alt="Dynamic chart" /></td>
<td><img src="chart.png" alt="Dynamic chart" /></td>
</tr>
<tr>
<td>$\Delta$Photolysis</td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
<td><img src="chart.png" alt="Photolysis chart" /></td>
</tr>
<tr>
<td>$\Delta$Total</td>
<td><img src="chart.png" alt="Total chart" /></td>
<td><img src="chart.png" alt="Total chart" /></td>
<td><img src="chart.png" alt="Total chart" /></td>
<td><img src="chart.png" alt="Total chart" /></td>
<td><img src="chart.png" alt="Total chart" /></td>
<td><img src="chart.png" alt="Total chart" /></td>
<td><img src="chart.png" alt="Total chart" /></td>
</tr>
</tbody>
</table>
Figure 8: Vertical profile of integrated reaction rates in JJJ at noon (full-layer heights above ground are 40, 96, 160, 241, 355, 503, 688, 884, 1100, 1357 m; Baseline is the simulation in SimBL; ΔDynamic is the difference between SimSF and SimNF; ΔPhotolysis is the difference between SimNF and SimBL; ΔTotal is the difference between SimSF and SimBL; $P_{\text{totOx}}$ is total O$_x$ production rate, unit: ppb hr$^{-1}$; OH CL is OH chain length; $P_{\text{NewOH}}$ is the production rate of new OH, unit: ppb hr$^{-1}$; $P_{\text{ReactedOH}}$ is the production rate of reacted OH, unit: ppb hr$^{-1}$; $P_{\text{H2O2}}$ is the production rate of H$_2$O$_2$, unit: ppb hr$^{-1}$; $P_{\text{HNO3}}$ is the production rate of HNO$_3$, unit: ppb hr$^{-1}$; the ratio of $P_{\text{H2O2}}/P_{\text{HNO3}}$ is only shown for layer 1-5)