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# Summertime ozone formation in Xi'an and surrounding areas, China

T. Feng<sup>1,2,3</sup>, N. Bei<sup>1,2</sup>, R. Huang<sup>2,4</sup>, J. Cao<sup>2,3</sup>, Q. Zhang<sup>5</sup>, W. Zhou<sup>3</sup>, X. Tie<sup>2,3</sup>, S. Liu<sup>2,3</sup>, T. Zhang<sup>2,3</sup>, X. Su<sup>2,3</sup>, W. Lei<sup>6</sup>, L. T. Molina<sup>6</sup>, and G. Li<sup>2,3</sup>

<sup>1</sup>School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an, China <sup>2</sup>Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China

<sup>3</sup>State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China

<sup>4</sup>Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), Villigen, Switzerland

<sup>5</sup>Department of Environmental Sciences and Engineering, Tsinghua University, Beijing, China <sup>6</sup>Molina Center for Energy and the Environment, La Jolla, CA, USA

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Correspondence to: G. Li (ligh@ieecas.cn)

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#### Abstract

In the study, the ozone ( $O_3$ ) formation is investigated in Xi'an and surrounding areas, China using the WRF-CHEM model during the period from 22 to 24 August 2013 corresponding to a heavy air pollution episode with high concentrations of  $O_3$  and  $PM_{2.5}$ 

- <sup>5</sup> (particulate matter with aerodynamic diameter less than 2.5 μm). The WRF-CHEM model generally performs well in simulating the surface temperature and relative humidity compared to the observations and also reasonably reproduces the observed temporal variations of the surface wind speed and direction. The convergence formed in Xi'an and surrounding areas is favorable for the accumulation of pollutants, causing
- <sup>10</sup> high concentrations of O<sub>3</sub> and PM<sub>2.5</sub>. In general, the calculated spatial patterns and temporal variations of near-surface O<sub>3</sub> and PM<sub>2.5</sub> are consistent well with the measurement at the ambient monitoring stations. The simulated daily mass concentrations of aerosol constituents, including sulfate, nitrate, ammonium, elemental and organic carbon, are also in good agreement with the filter measurements. High aerosol concen-
- <sup>15</sup> trations in Xi'an and surrounding areas significantly decrease the photolysis frequencies and can reduce near-surface  $O_3$  concentrations by more than  $50 \,\mu gm^{-3}$  (around 25 ppb) on average. Sensitivity studies show that the  $O_3$  production regime in Xi'an and surrounding areas is complicated, varying from NO<sub>x</sub> to VOC-sensitive chemistry. The industry emissions contribute the most to the  $O_3$  concentrations compared to the nat-
- <sup>20</sup> ural and other anthropogenic sources, but still do not play a determined role in the O<sub>3</sub> formation. The complicated O<sub>3</sub> production regime and high aerosol levels constitute a dilemma for O<sub>3</sub> control strategies in Xi'an and surrounding areas. In the condition with high O<sub>3</sub> and PM<sub>2.5</sub> concentrations, decreasing various anthropogenic emissions cannot efficiently mitigate the O<sub>3</sub> pollution, and a 50 % reduction of all the anthropogenic emissions canemissions only decreases near-surface O<sub>3</sub> concentrations by less than 14 % during
- <sup>25</sup> emissions only decreases near-surface  $O_3$  concentrations by less than 14% during daytime. Further studies need to be performed for  $O_3$  control strategies considering manifest changes of the emission inventory and uncertainties of meteorological field simulations.



### 1 Introduction

Ozone (O<sub>3</sub>) is a key species in the atmosphere due to its controlling role in the photochemistry in the stratosphere and troposphere (Seinfeld and Pandis, 2006) since O<sub>3</sub> and its photochemical derivative, OH, are the key oxidants for most reduced gases
<sup>5</sup> (Brasseur et al., 1999). Atmospheric O<sub>3</sub> also contributes to the global climate change because of absorption of the infrared radiation, constituting one of the important short-lived climate pollutants. Additionally, high levels of surface O<sub>3</sub> exert deleterious impacts on ecosystems and human health (Cao et al., 2012; Zhou et al., 2011) and thence O<sub>3</sub> becomes one of the criteria pollutants regulated by the environmental agencies in many countries, such as US Environmental Protection Agency (US EPA) and the China's Ministry of Environmental Protection (China MEP).

Rapid industrialization and urbanization have caused severe air pollution recently in China (e.g., De Smedt et al., 2010; Lu et al., 2011) and numerous studies have been performed to investigate the severe  $O_3$  pollution, particularly in the Beijing–Tianjin-

- <sup>15</sup> Hebei region (e.g., Wang et al. 2006; Lin et al., 2008; Tang et al., 2009; Xu et al., 2011), Yangtze Delta region (e.g., Geng et al., 2009, 2011; Tie et al., 2009, 2012), and Pearl River Delta region (e.g., Zhang et al., 2008; T. Wang et al., 2009; Cheng et al., 2010; Wang et al., 2011; Li et al., 2013). For example, T. Wang et al. (2006) have observed strong O<sub>3</sub> production in urban plumes from Beijing with a maximum O<sub>3</sub> con-
- <sup>20</sup> centration of 286 ppb. Using a chemical transport model, Tie et al. (2009) have shown that unfavorable meteorological conditions cause high near-surface  $O_3$  level exceeding 100 ppb in the Shanghai region. T. Wang et al. (2009) have reported increasing surface  $O_3$  concentrations in the background atmosphere of Southern China during the period from 1994 to 2007.
- As the largest city in northwestern China with the population of more than 8 million, Xi'an is located in the Guanzhong basin. The basin is nestled between the Qinling Mountains in the south and the Loess Plateau in the north, with a warm-humid climate. The unique topography is not favorable for the dispersion of air pollutants (Fig. 1a)



and, with the rapid increasing industries and city expansions, heavy air pollutions often attack the basin (Cao et al., 2005; Shen et al., 2008, 2009). Shen et al. (2009) have reported that the  $PM_{2.5}$  (particulate matter with aerodynamic diameter less than 2.5 µm) mass concentrations in Xi'an exceed 350 µgm<sup>-3</sup> during haze episodes and the straw combustion in suburban area of Xi'an increases  $PM_{2.5}$  level to 400 µgm<sup>-3</sup>. However, studies on O<sub>3</sub> measurements and formation mechanism in Xi'an are still limited until now. X. Wang et al. (2012) have performed one-year surface O<sub>3</sub> measurement at an urban site in Xi'an in 2008. They have shown high O<sub>3</sub> episodes with the O<sub>3</sub> concentration of more than 100 ppb in May and June and found that high O<sub>3</sub> episodes are associated with biogenic emissions from Qinling Mountains. Hence, considering the increasingly stringent air quality standards in China, studies are imperative to verify the O<sub>3</sub> and other pollutants formation from both natural and anthropogenic emission sources to support the design and implementation of emission control strategies in the

Since January 2013, the China MEP has commenced to release the real-time hourly

observations of chemical species at the national ambient monitoring stations, includ-

ing  $O_3$ ,  $NO_2$ , CO,  $SO_2$ ,  $PM_{2.5}$ , and  $PM_{10}$  (particulate matter with aerodynamic diameter less than 10 µm). Total thirteen national monitoring stations are distributed at the

nine districts in Xi'an. In addition, continuous measurements of aerosol mass, chemical composition, and optical properties have been conducted at the Institute of Earth

Environment, Chinese Academy of Sciences (IEECAS) in Xi'an, China since 2003. All

those measurements provide an opportunity to investigate  $O_3$  formation in Xi'an and surrounding areas. The purpose of the present study is to evaluate the  $O_3$  formation

from anthropogenic and natural sources and the difficulties in the O<sub>3</sub> control strategy

caused by the complicated nonlinear formation of O<sub>3</sub> and the aerosol impact on the

photochemistry. The WRF-CHEM model and the model configuration are described

in Sect. 2. Results of the modeling experiments and comparisons are presented in

Sect. 3, and the Conclusions are given in Sect. 4.

Guanzhong basin.

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**Discussion** Paper ACPD 15, 30563-30608, 2015 Summertime ozone formation in Xi'an and surrounding **Discussion** Paper areas, China T. Feng et al. **Title Page** Introduction Abstract Discussion Paper Conclusions References **Figures** Tables Back Close **Discussion** Paper Full Screen / Esc **Printer-friendly Version** Interactive Discussion

#### 2 Model and method

#### 2.1 WRF-CHEM model

In this study, a specific version of the WRF-CHEM model (Grell et al., 2005) is applied to verify the  $O_3$  formation in Xi'an and surrounding areas, which is developed by Li et

- al. (2010, 2011a, b, 2012) at the Molina Center for Energy and the Environment, with a new flexible gas phase chemical module and the CMAQ (version 4.6) aerosol module developed by US EPA (Binkowski and Roselle, 2003). The wet deposition follows the method used in the CMAQ and the dry deposition of chemical species is parameterized following Wesely (1989). The photolysis rates are calculated using the FTUV (Tie et al., 2003; Li et al., 2005) in which the impacts of aerosols and clouds on the photochemistry
- 2003; Li et al., 2005) in which the impacts of aerosols and clouds on the photochemistry are considered (Li et al., 2011a).

We utilize ISORROPIA Version 1.7 (http://nenes.eas.gatech.edu/ISORROPIA/) to simulate the inorganic aerosols in the WRF-CHEM model. The inorganic aerosol module calculates the composition and phase state of an ammonium-sulfate-nitrate-

- <sup>15</sup> chloride-sodium-calcium-potassium-magnesium-water inorganic aerosol in thermodynamic equilibrium with gas phase precursors. In the present study, the module is primarily used to predict the thermodynamic equilibrium between the ammonia-sulfatenitrate-chloride-water aerosols and their gas phase precursors of H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>-NH<sub>3</sub>-HCI-water vapor.
- The secondary organic aerosol (SOA) formation is predicted using a non-traditional SOA module. The module includes the volatility basis-set (VBS) modeling method in which primary organic components are assumed to be semi-volatile and photochemically reactive and are distributed in logarithmically spaced volatility bins (Li et al., 2011b). Nine surrogate species with saturation concentrations from 10<sup>-2</sup> to 10<sup>6</sup> µg m<sup>-3</sup>
- at room temperature are used for the primary organic aerosol (POA) components following the approach of Shrivastava et al. (2008). Detailed description about the volatility basis-set approach can be found in Li et al. (2011b). The contributions of glyoxal and methylglyoxal to the SOA formation are also included in the SOA module. The SOA



formation from glyoxal and methylglyoxal is parameterized as a first-order irreversible uptake by aerosol particles, with a reactive uptake coefficient of  $3.7 \times 10^{-3}$  for glyoxal and methylglyoxal (Zhao et al., 2006; Volkamer et al., 2007).

### 2.2 Model configuration

- <sup>5</sup> A three-day episode from 22 to 24 August 2013 is selected in the study, representing a heavy air pollution event in Xi'an and surrounding areas with high levels of O<sub>3</sub> and PM<sub>2.5</sub>. The WRF-CHEM model is configured with grid spacing of 3 km (201 × 201 grid points) centered at 34.25° N and 109° E (Fig. 1a). Thirty-five vertical levels are used in a stretched vertical grid with spacing ranging from 50 m near the surface,
- to 500 m at 2.5 km a.g.l. and 1 km above 14 km. The modeling system employs the microphysics scheme of Lin et al. (1983), the MYJ TKE planetary boundary layer scheme (Janjic, 2002), the MYJ surface layer scheme (Janjic, 2002), the Unified Noah land-surface model (Chen and Dudhia, 2000), the RRTM longwave radiation parameterization (Mlawer et al., 1997), and the Goddard shortwave module (Chou and Suarez, 1994). Meteorological initial and boundary conditions are obtained from NCEP
- 1° × 1° reanalysis data. Chemical initial and boundary conditions are obtained from MOZART 6-h output (Horowitz et al., 2003). For the episode simulations, the spin-up time of the WRF-CHEM model is one day.

The SAPRC 99 chemical mechanism is utilized in simulations. The anthropogenic emission inventory (EI) used in the present study is developed by Q. Zhang et al. (2009), including contributions from agriculture, industry, power, residential and transportation sources (Fig. 2). High emissions of volatile organic compounds (VOCs) and nitrogen oxide ( $NO_x$ ) are concentrated in Xi'an and surrounding areas. The primary organic aerosol emissions are redistributed following the study of Tsimpidi et al. (2010).

<sup>25</sup> Additionally, the biogenic emissions are calculated on-line with the WRF-CHEM model using the MEGAN model (Guenther et al., 2006).



#### 2.3 Statistical methods for comparisons

In the study, the mean bias (MB), the root mean square error (RMSE), and the index of agreement (IOA) are used to evaluate the WRF-CHEM model simulations of meteorological parameters, gas-phase species, and aerosols.

5 MB = 
$$\frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)$$

$$\text{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N} (P_i - O_i)^2\right]^{\frac{1}{2}}$$

$$IOA = 1 - \frac{\sum_{i=1}^{N} (P_i - O_i)^2}{\sum_{i=1}^{N} (|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$$

where  $P_i$  and  $O_i$  are the simulated and observed variable, respectively. N is the total 10 number of the predictions used for comparisons, and  $\bar{P}$  and  $\bar{O}$  denotes the average of the prediction and observation, respectively. IOA ranges from 0 to 1, with 1 indicating perfect agreement between model and observation.

#### **Results and discussion** 3

#### Model performance 3.1 15

For the discussion convenience, we define the reference simulation in which the emissions from various sources and aerosol effects on the photochemistry are included



(1)

(2)

(3)

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(hereafter referred to as REF), and results in the reference simulation are compared with the observations in Xi'an.

### 3.1.1 Meteorological fields simulations

Considering that the meteorological conditions play a key role in air pollution simulations (Bei et al., 2008, 2010, 2012), which determine the accumulation or dispersion of pollutants, verifications are first performed for the simulations of meteorological fields in Xi'an and surrounding areas. Figure 3 shows the temporal profiles of the simulated and observed surface temperature and relative humidity averaged over six meteorological observation sites from 22 to 24 August 2013. The WRF-CHEM model reproduces successfully the temporal variations of the surface temperature during the three-day episode, but the model slightly underestimates the observations generally, particularly in the morning (Fig. 3a). The MB and RMSE are -0.76 and 1.0 °C, respectively, and the IOA reaches 97 %, indicating a good agreement of the surface temperature sim-

ulations with measurements (Table 1). The WRF-CHEM model generally tracks the temporal variations of the surface relative humidity well, with the IOA of 0.92 (Fig. 3b). However, model underestimation of the observed surface relative humidity is obvious during midnight and morning. The MB and RMSE is -4.5 and 5.5% for the surface relative humidity simulations, respectively.

Figures 4 and 5 present the comparisons of simulated and observed wind speeds and directions at six meteorological observation sites from 22 to 24 August 2013, respectively. The WRF-CHEM model fails to yield the observed temporal variation of the wind speed at Xi'an site with the IOA of 0.26, and also significantly overestimates the observation, with the MB of 1.7 m s<sup>-1</sup> and RMSE of 2.1 m s<sup>-1</sup>. In addition, the observed wind direction is variable at Xi'an site, but the simulated winds withhold the northeast until the evening on 23 August, and then change to the southwest before the noontime on 24 August. As the Xi'an site is located in the urban center of Xi'an, it is surrounded by high buildings which significantly alter the air flow at the ground surface, causing light and disordered surface winds. Although the urban canopy model is utilized in the



WRF-CHEM model simulations, the simulated surface winds are still biased considerably in the urban region due to the simplification of building distributions and heights and the incapability of the model in micro-scale simulations. The simulated winds at Xi'an site are similar to those at Lintong, Xianyang, and Jinghe sites in the north of

- Si'an, but in general, the wind simulations at these three sites are in good agreement with the observations, with the IOA of at least 0.61 for the wind speed, further showing the impacts of buildings in the urban region on the wind simulations. The WRF-CHEM model performs reasonably in predicting the wind speed and direction at Chang'an and Lantian sites in the south of Xi'an. It should be noted that the model considerably
- <sup>10</sup> overestimates the observed wind speeds at all observations sites in the early morning on 23 August and also fails to track the variation of wind directions over the sites in the south of Xi'an, which causes the biased dispersion of the plume formed during daytime. In addition, the overestimation of the wind speed is also remarkable in the afternoon and evening on 24 August, which evacuates the plume formed in the urban <sup>15</sup> region more efficiently.

#### 3.1.2 Gas-phase species simulations

The modeled O<sub>3</sub> and NO<sub>2</sub> mass concentrations are compared to the measurements at ambient monitoring stations released by the China MEP. Considering the dominant influence of meteorological fields on air pollution modeling, Fig. 6 provides the spatial distributions of calculated and observed near-surface O<sub>3</sub> concentrations at 08:00 and 15:00 Beijing Time (BJT) from 22 to 24 August 2013, along with the simulated wind fields. When the northeast wind is prevalent in the Guanzhong basin, due to the impact of the topography (Fig. 1), the stagnant conditions are frequently formed in Xi'an and surrounding areas. At 08:00 BJT, the WRF-CHEM model is subject to underestimate the observed near-surface O<sub>3</sub> concentrations in the urban area of Xi'an, which perhaps is caused by the titration of emitted NO from traffic during rush hours. At 15:00 BJT, the calculated near-surface O<sub>3</sub> distributions are generally consistent well with the obser-



and the stagnant region with the high  $O_3$  plume locates in the southwest of Xi'an and surrounding areas, so the predicted near-surface  $O_3$  concentrations are not more than 160 µgm<sup>-3</sup> in the urban area of Xi'an, and are in good agreement with measurements. On August 23, the convergence in the urban area of Xi'an is favorable for the accumulation of  $O_3$  precursors and the high  $O_3$  plume is formed in the afternoon, with the near-surface  $O_3$  concentration exceeding 200 µgm<sup>-3</sup>. On August 24, the plume formed in the urban region of Xi'an is pushed to the north of Xi'an and surrounding areas in the afternoon and the simulated near-surface  $O_3$  concentrations are less than 200 µgm<sup>-3</sup> in the urban area of Xi'an, generally consistent with the observations. In addition, the

- $O_3$  level in Xi'an and surrounding areas is also affected by the  $O_3$  transport from its upwind region. It is worth to note that the WRF-CHEM model cannot well replicate the spatial variation of the observed near-surface  $O_3$  concentration at monitoring sites in the urban area of Xi'an. Although the 3 km horizontal resolution is used in the study, it still cannot well resolve the spatial variation of near-surface  $O_3$  concentrations over
- <sup>15</sup> monitoring sites with the distance of less than 21 km (Skamarock, 2004). However, unfortunately, the ambient monitoring sites in Xi'an are mainly concentrated in the urban area with around 20 km width and 30 km length, so future model studies with the higher horizontal resolution need to be performed to improve the near-surface O<sub>3</sub> simulations under the present monitoring site distribution. The simulated near-surface NO<sub>2</sub> distri-
- <sup>20</sup> butions agree well with the observations at the ambient monitoring sites in the morning (Fig. 7a, c, and e), with the highest NO<sub>2</sub> concentration in the urban center of Xi'an. In the afternoon, the WRF-CHEM model overstates the observation in the urban center on 23 August and underestimates on 24 August.

Figure 8 displays the diurnal profiles of predicted and observed near-surface O<sub>3</sub> and NO<sub>2</sub> concentrations averaged over the ambient monitoring sites during the episode. The WRF-CHEM model tracks the temporal variations of surface O<sub>3</sub> concentrations well during daytime (Fig. 8a), but the simulated near-surface O<sub>3</sub> concentrations deviates markedly from the observations in the early morning on 23 August. Apparently, the plume with high O<sub>3</sub> concentrations formed in the southwest of Xi'an during daytime



(Fig. 6b) on 22 August is transported back to the urban area of Xi'an in the early morning on 23 August, causing the observed high near-surface  $O_3$  level. However, due to biases of the wind simulations in the early morning on 23 August (Figs. 4 and 5), the plume formed on the previous day is not transported back to the urban area of Xi'an,

- leading to the remarkable underestimation of the observed O<sub>3</sub> concentrations. The MB, RMSE, and IOA of the simulated near-surface O<sub>3</sub> concentration averaged over monitoring stations are -9.0, 29, and 0.91 μgm<sup>-3</sup>, respectively. Although the WRF-CHEM model reasonably well produces the variation of observed near-surface NO<sub>2</sub> concentrations (Fig. 8b), with the IOA of 0.73, it often overestimates or underestimates the observation. Uncertainties of simulated meteorological fields or the emission inventory might constitute the possible reasons for the model biases in simulating NO.
- might constitute the possible reasons for the model biases in simulating NO<sub>2</sub> distributions and variations.

In general, the calculated distribution and variation of near-surface  $O_3$  and  $NO_2$  concentrations are in good agreement with the corresponding observations, showing that

the WRF-CHEM model well simulates the meteorological fields and the emission inventory used in the study is also reasonable.

#### 3.1.3 Aerosol simulations

Atmospheric particular matter or aerosols scatter or absorb a fraction of solar radiation and increase or decrease the photolysis rates in the atmosphere, influencing the  $O_3$  for-

- <sup>20</sup> mation. Therefore, in order to reasonably verify the aerosol impact on photolysis and O<sub>3</sub> level, it is imperative to evaluate the simulated aerosol constituents, variation and distribution using available measurements. Daily measurement of aerosol constituents is performed using the filter sample at IEECAS site, including sulfate, nitrate, ammonium, organic and elemental carbon. Figure 9a presents a scatterplot of the measured versus
- <sup>25</sup> calculated daily mean concentration of aerosol constituents at IEECAS site from 22 to 24 August 2013. It should be noted that the simulated organic aerosol is compared with the filter measured organic carbon scaled by a factor of 2 (Carlton et al., 2010). The WRF-CHEM model exhibits good performance in modeling daily mean sulfate, and or-



ganic aerosol concentrations. The model tends to overestimates the observed nitrate and ammonium concentration, which might be caused by the nitrate loss due to the evaporation from filters in summer (lanniello et al., 2011). The simulated daily mean elemental carbon concentrations deviate from the measurements considerably on 22

- and 23 August, which is perhaps caused by the daily variations of elemental carbon emissions. The comparison of observed and modeled PM<sub>2.5</sub> mass composition averaged during the 3-day episode is displayed in Fig. 9b and c. Sulfate is the dominant constituent of the observed PM<sub>2.5</sub> at IEECAS site, consisting of around 39% of the PM<sub>2.5</sub> mass, and the simulated sulfate contribution to the PM<sub>2.5</sub> mass is about 35%
- on average, closed to the observation. The high sulfate concentrations come mainly from the SO<sub>2</sub> heterogeneous reaction on aerosol surfaces under humid conditions. The measured and modeled organic aerosols make up about 19% of the PM<sub>2.5</sub> mass at the IEECAS site, and secondary organic aerosol contributes more than 50% of the modeled organic aerosol due to the high atmospheric oxidation capacity in summer. The measured area prime pittete and elemental earlier exercise area and allocations.
- <sup>15</sup> The modeled ammonium, nitrate, and elemental carbon account for about 15, 6.8, and 3.1 % of the  $PM_{2.5}$  mass, respectively, comparable to the observed 14, 6.6, and 3.6 % at IEECAS site.

Figure 10 shows the simulated geographic distributions of near-surface  $PM_{2.5}$  mass concentrations with observations over monitoring stations at 08:00 and 15:00 BJT from

- <sup>20</sup> 22 to 24 August. On 22 August, the convergence is formed in the north of Xi'an and surrounding areas at 08:00 BJT, causing the buildup of pollutants and high  $PM_{2.5}$  concentrations. The simulated near-surface  $PM_{2.5}$  concentrations are more than 75 µg m<sup>-3</sup> in the north of Xi'an and surrounding areas, consistent with the measurements, but exceed 150 µg m<sup>-3</sup> in the south part where the stagnant conditions are formed, much bisher than the absorbation.
- <sup>25</sup> higher than the observation. At 15:00 BJT, well organized northeast winds push the convergence zone to the southeast of Xi'an and surrounding areas and the simulated near-surface  $PM_{2.5}$  concentrations are less than 75 µg m<sup>-3</sup>, in good agreement with the measurements. On 23 August, the convergence is withheld in the urban area of Xi'an, causing the heavy  $PM_{2.5}$  pollution. The calculated  $PM_{2.5}$  concentration is more than



115 μg m<sup>-3</sup> at 08:00 and 15:00 BJT, comparable to the measurements. The observed and simulated PM<sub>2.5</sub> patterns on 23 August are similar to those on 22 August, but the PM<sub>2.5</sub> concentrations on 24 August are enhanced. For example, all the observed and simulated PM<sub>2.5</sub> concentrations over monitoring stations exceed 150 μg m<sup>-3</sup> at 08:00 BJT. In addition, at 15:00 BJT, due to the overestimation of the wind speed (Fig. 4), the convergence zone is pushed to the south of Xi'an and surrounding areas, causing the underestimation of near-surface PM<sub>2.5</sub> concentration in the north part. The WRF-CHEM model reproduces the observed diurnal profile of the near-surface PM<sub>2.5</sub> concentration averaged over the monitoring stations during the episode (Fig. 11), with

- <sup>10</sup> the MB of  $-1.4 \mu g m^{-3}$ , the RMSE of  $21 \mu g m^{-3}$ , and the IOA of 0.92. Apparently, the convergence zone location, which is determined by the meteorological fields, significantly influences the PM<sub>2.5</sub> simulations. When the simulated convergence zone is formed in the south of Xi'an and surrounding areas in the morning on 22 August, the WRF-CHEM model considerably overestimates the observed PM<sub>2.5</sub> concentration.
- However, if the simulated winds are too strong and the convergence zone is pushed to the south of Xi'an and surrounding areas on 24 August, the model notably underestimates the observations.

The simulated column-integrated aerosol optical depth (AOD) and single scattering albedo (SSA) are verified using the available measurements from the surface site and satellite. The simulated aerosol optical properties are calculated using the method developed by Li et al. (2011a). Figure 12a and b displays the comparison of simulations of the column-integrated AOD and aerosol SSA at 440 nm with measurements at IEECAS site, respectively, which is retrieved from the observations of a sun-sky radiometer (Su et al., 2014). The simulated AOD on 22 August is comparable to the measurements at IEECAS site, but the WRF-CHEM model overestimates the observation in the morning due to the overestimation of PM<sub>2.5</sub> concentrations. The simulated SSA on 22 August





to the measurements on 23 August (Fig. 6), so the underestimation of the relative humidity, not limited to the ground surface as shown in Fig. 4, might constitute one of the most possible reasons for the underestimation of the AOD and aerosol SSA. The distribution of the calculated AOD at 550 nm from MODIS (Moderate Resolution Imaging

- <sup>5</sup> Spectroradiometer) aerosol level-2 product at 5 × 5 1-km pixel resolution is also compared with the model results (Fig. 12c and d). The simulated AOD pattern on 22 August is in good agreement with the measurements, except over the Qinling Mountains where the convection is active. The WRF-CHEM model underestimates the observed AOD in the north of Xi'an on 23 August, which is likely caused by the bias of the simulated rel-
- <sup>10</sup> ative humidity. Apparently, the AOD at 550 nm in Xi'an and surrounding areas is high, exceeding 0.8 on 22 August and 1.0 on 23 August.

### 3.2 Sensitivity studies

# 3.2.1 Effects of aerosol on the O<sub>3</sub> formation

O<sub>3</sub> formation in the atmosphere is a complicated photochemical process, which is de termined by its precursors from various sources and transport in the presence of sun light. High AOD in Xi'an and surrounding areas efficiently scatter or absorb sunlight to decrease the photolysis frequencies in the planetary boundary layer (PBL) and further the O<sub>3</sub> formation. High O<sub>3</sub> levels enhance atmospheric oxidation capability and the secondary aerosol formation, increasing the aerosol concentration in the atmosphere, but
 conversely, high aerosol levels decrease the photolysis frequencies and suppress the O<sub>3</sub> formation in the PBL. The interactions of O<sub>3</sub> with aerosols complicate the design of O<sub>3</sub> control strategies.

The aerosol effect on the O<sub>3</sub> formation in Xi'an and surrounding areas is examined by the sensitivity study without aerosol effects on the photolysis compared to the reference simulation (hereafter we define the sensitivity simulation as SEN). Figure 13 presents the diurnal profiles of the change of the NO<sub>2</sub> photolysis frequency (*J*[NO<sub>2</sub>]) and O<sub>3</sub> concentration averaged in Xi'an and surrounding areas due to aerosol effects from 22



to 24 August, respectively. Aerosols significantly decrease  $J[NO_2]$  by 30–70 % (defined as (SEN-REF)/SEN) in the early morning and late afternoon when the solar zenith angle is large, showing the impact of long aerosol optical path for incoming radiation. Due to the high aerosol level, the aerosol effect on  $J[NO_2]$  is still remarkable during noontime, decreasing  $J[NO_2]$  by over 20% on 23 and 24 August when the plume is stagnant in the urban region of Xi'an. The aerosol effect on the photolysis frequency in the study is more significant than those reported by previous studies (e.g., Jacobson, 1998; Castro et al., 2001; Li et al., 2005, 2011a). The aerosol impact on  $O_3$  formation is the most significant in the late morning and early afternoon (Fig. 13b). On average, in Xi'an and surrounding areas, the reduction of O<sub>3</sub> concentration (defined as (SEN-REF)) due to 10 aerosol effect on photolysis are not more than  $20 \,\mu g \,m^{-3}$  on 22 August, but the O<sub>3</sub> concentrations are decreased by more than  $30 \,\mu g \,m^{-3}$  during noontime on 23 August and over  $50 \mu g m^{-3}$  in the late morning on 24 August. The aerosol effect on O<sub>3</sub> formation in the study is comparable to those reported by Castro et al. (2001) in Mexico City. It should be noted that the impact of photolysis on O<sub>3</sub> level varies depending on the 15

ratio of VOCs to  $NO_x$  (Stockwell and Goliff, 2004). Apparently, the remarkable aerosol effects on  $O_3$  formation cause a predicament for  $O_3$  control strategies. If  $O_3$  concentrations are decreased through reducing its precursors emissions, the aerosol level is also decreased due to direct and indirect contributions from the emission control, which compensates the  $O_3$  decrease by enhancing the photolysis frequency.

# 3.2.2 O<sub>3</sub> response to emission changes

In the urban area, when the meteorological conditions are favorable for the accumulation of pollutants in the PBL, the  $O_3$  precursors of anthropogenically or naturally emitted VOCs and  $NO_x$ , react chemically in the presence of sunlight, causing the high  $O_3$  level.

<sup>25</sup> In order to devise the O<sub>3</sub> control strategy, it is imperative to investigate the regime of O<sub>3</sub> production. The regime of O<sub>3</sub> production in Xi'an and surrounding areas is examined using the sensitivity studies through reducing anthropogenic VOCs (AVOCs) or NO<sub>x</sub>



emissions by 50% in the WRF-CHEM simulations. Figure 14 shows the comparison of near-surface  $O_3$  concentrations averaged in the urban area of Xi'an in the reference simulation to the two sensitivity studies in which AVOCs and NO<sub>x</sub> are decreased by 50%, respectively. A 50% reduction of AVOCs decreases the  $O_3$  concentration av-

- <sup>5</sup> eraged in Xi'an surrounding areas consistently during the episode, particularly during peak time (defines as 14:00–16:00 BJT hereafter). A 50 % reduction of NO<sub>x</sub> enhances the near-surface O<sub>3</sub> level in the morning due to the emission decrease of NO, but in the afternoon, it decreases the near-surface O<sub>3</sub> level, same as the effect from a 50 % reduction of AVOCs, leading to a complicated O<sub>3</sub> production regime.
- <sup>10</sup> Figure 15a shows the 3-day average near-surface O<sub>3</sub> change during peak time with a 50 % reduction in NO<sub>x</sub> emissions (defined as O<sub>3</sub>(SEN) – O<sub>3</sub>(REF)). In the Xi'an and surrounding areas, except the urban center, the simulated average near-surface O<sub>3</sub> concentrations are decreased by about 10–40  $\mu$ gm<sup>-3</sup> due to a 50 % reduction of NO<sub>x</sub>. The near-surface O<sub>3</sub> concentrations are only enhanced in the urban center of Xi'an with
- <sup>15</sup> very high NO<sub>x</sub> emissions, but less than 10  $\mu$ gm<sup>-3</sup>. A 50 % reduction of AVOCs emissions consistently reduces the near-surface O<sub>3</sub> concentration in Xi'an and surrounding areas by up to 40  $\mu$ gm<sup>-3</sup> (Fig. 15b). Apparently, the response of O<sub>3</sub> change to a 50 % reduction of NO<sub>x</sub> or AVOCs emissions cannot obviously indicate the O<sub>3</sub> production regime in Xi'an and surrounding areas. Sillman (1995) proposed that the ratio of the
- <sup>20</sup> production rates of hydrogen peroxide and nitric acid  $(H_2O_2/HNO_3)$  can be used to investigate VOC-NO<sub>x</sub> sensitive photochemistry. If the ratio is less than 0.3, the O<sub>3</sub> production regime is VOC sensitivity. If the ratio exceeds 0.5, the regime is NO<sub>x</sub> sensitivity. The ratio ranging from 0.3 to 0.5 indicates the transition from NO<sub>x</sub> to VOC-sensitive chemistry. Figure 15c displays the distribution of the 3-day average  $H_2O_2/HNO_3$  during
- <sup>25</sup> the O<sub>3</sub> peak time. In Xi'an and surrounding areas, the  $H_2O_2/HNO_3$  ratio varies from 0.2 to 1.0, showing that the O<sub>3</sub> production regime is very complicated. In the south of Xi'an and surrounding areas, the O<sub>3</sub> production regime lies in the transition from NO<sub>x</sub> to VOC-sensitive chemistry. The analyses using  $H_2O_2/HNO_3$  indicator and the results



obtained from the two sensitivity studies indicated that it is not straightforward to devise an effective  $O_3$  control strategy for Xi'an and surrounding areas.

## 3.2.3 O<sub>3</sub> contribution from natural and anthropogenic sources

Biogenic emissions provide natural O<sub>3</sub> precursors and many studies have shown that naturally emitted VOCs play an important role in ground-level O<sub>3</sub> in urban areas (e.g., Solmon et al., 2004; Li et al., 2006). So biogenic emissions constitute a background  $O_3$  source which can not be controlled anthropogenically, complicating the  $O_3$  control strategy. A sensitivity study without the biogenic emissions is conducted and compared with the reference simulation to evaluate the  $O_3$  contribution from biogenic emissions. During noontime, the biogenic emissions contribute about 0.3 ppb isoprene averaged 10 in Xi'an and surrounding areas, and the  $O_3$  contribution from biogenic emissions is around 10  $\mu$ g m<sup>-3</sup> (Fig. 16). Large amounts of biogenic emissions are released over the Qinling Mountains in the north of Xi'an, and can be transported to the urban area under favorable meteorological conditions to enhance  $O_3$  formation. However, the northeast wind is prevalent in the Guanzhong basin during daytime, which is not favorable for 15 the transport of biogenic emissions from the Qinling Mountains. Although the O<sub>3</sub> level enhanced by biogenic emissions is not significant in Xi'an and surrounding areas, the high reactivity of naturally emitted VOCs, such as isoprene and monoterpenes, still play a role in the O<sub>3</sub> formation when the anthropogenic VOCs are decreased for the O<sub>3</sub> control strategy. 20

We have further used the sensitivity studies to evaluate the  $O_3$  contributions of anthropogenic emissions from industry, residential and transportation sources, respectively. The industry emissions contribute more than 70% of the anthropogenic VOCs, so play the most important role in the  $O_3$  formation in Xi'an and surrounding areas during daytime, compared to residential and transportation emissions. On average, the near-surface  $O_3$  contribution from the industry emissions is about 10–30 µg m<sup>-3</sup> in the

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afternoon and exceeds  $20 \mu \text{gm}^{-3}$  during O<sub>3</sub> peak time (Fig. 17b). The near-surface

 $O_3$  contribution from the transportation emissions ranges from 10 to  $20 \,\mu g \,m^{-3}$  in the afternoon, and the residential emissions play a nonnegligible role in the O<sub>3</sub> formation, with the near-surface  $O_3$  contribution less than  $10 \,\mu g \,m^{-3}$ .

- Sensitivity studies have shown that there is no an individual anthropogenic emission <sup>5</sup> source which dominates the O<sub>3</sub> level in Xi'an and surrounding areas. The simulation without the most important industry source still predicts high near-surface O<sub>3</sub> concentrations in Xi'an and surrounding areas (Fig. 17a). The O<sub>3</sub> production regime in Xi'an and surrounding areas varies from NO<sub>x</sub> to VOC-sensitive chemistry, constituting one of the possible reasons for the insensitivity of  $O_3$  concentration to the emission change.
- Additionally, in case of high aerosol levels, aerosol effects on photolysis also compen-10 sate the O<sub>3</sub> decrease through enhancing photolysis frequencies due to decrease of aerosol concentrations caused by the emission reduction. Although the biogenic emission does not play a key role in the O<sub>3</sub> formation in Xi'an and surrounding areas, it still provides reactive VOCs to precipitate the  $O_3$  formation. Therefore, under the sit-
- uation with high O<sub>3</sub> and PM<sub>2.5</sub> in Xi'an and surrounding areas, decreasing emissions 15 from various anthropogenic sources cannot efficiently mitigate the O<sub>3</sub> pollution. Sensitivity studies have been performed to further demonstrate the difficulties in devising O<sub>3</sub> control strategies through decreasing anthropogenic emissions from industry, residential, transportation, and all the anthropogenic sources by 50%, respectively in the WRF-CHEM simulations. A 50% reduction of the industry emissions only cause less 20
- than 7 % decrease of near-surface  $O_3$  concentrations in Xi'an and surrounding areas (Fig. 18). Even all the anthropogenic emissions are reduced by 50%, the decrease of near-surface O<sub>3</sub> concentrations is not more than 14%.

#### Summaries and conclusions 4

In the study, a 3-day episode with high  $O_3$  and  $PM_{2.5}$  concentrations from 22 to 24 Au-25 gust 2013, is simulated using the WRF-CHEM model to verify the O<sub>3</sub> formation in Xi'an and surrounding areas, China. The simulated surface temperatures are in good agree-



ment with the observations, with the MB of -0.76 °C, the RMSE of 1.0 °C, and the IOA of 97 %. The WRF-CHEM model generally tracks the temporal variations of the observed surface relative humidity, but is object to underestimate the observation. The model fails to reproduce the observed temporal variation of the wind speed and direc-

tion at an urban site, but generally performs reasonably in simulations of the surface wind speed and direction outside of the urban area of Xi'an.

When the northeast wind is prevalent in the Guanzhong basin, the specific topography of the basin causes convergence in Xi'an and surrounding areas, which is favorable for the accumulation of pollutants and the formation of heavy air pollutions. The WRF-CHEM model yields good simulations of the  $O_3$  distribution and variation in Xi'an

- <sup>10</sup> WRF-CHEM model yields good simulations of the  $O_3$  distribution and variation in Xi'an and surrounding areas compared to the observations. Although the model reproduces reasonably the observed NO<sub>2</sub> distribution and variation, it frequently overestimates or underestimates the observation.
- The simulated daily aerosol constituents, including sulfate, nitrate, ammonium, el-<sup>15</sup> emental and organic carbon, are consistent with the filter measurement at IEECAS site. The WRF-CHEM model reproduces well the pattern and variation of the observed PM<sub>2.5</sub> concentrations compared to the measurements at ambient monitoring stations. The modeled convergence zone location significantly influences the model performance in simulating the distribution and variation of PM<sub>2.5</sub> concentrations, show-
- ing the dominant influence of meteorological fields on air pollution simulations. The simulated column-integrated AOD at 550 nm and SSA at 440 nm are compared to the available measurements from the surface site and satellite. The calculated AOD and SSA agree well with the measurements on 22 August, but the AOD and SSA simulations are biased considerably on 23 August, which is perhaps caused by the underestimation of the relative humidity.

High aerosol levels significantly decrease the photolysis frequencies in Xi'an and surrounding areas. On average, the  $J[NO_2]$  at the ground surface is decreased by 30–70% in the early morning and late afternoon when the solar zenith angle is large, and even around noontime, the decrease of  $J[NO_2]$  is still significant, exceeding 20%



on 23 and 24 August. The aerosol effect on photolysis remarkably decreases the  $O_3$  formation in the late morning and early afternoon, with the  $O_3$  reduction of more than  $50 \,\mu g \,m^{-3}$  on average in Xi'an and surrounding areas. The remarkable aerosol effects on  $O_3$  formation complicate the devise of  $O_3$  control strategies. If the  $O_3$  mitigation causes the reduction of aerosols directly and indirectly, the enhanced photolysis due to the aerosol decrease compensates the  $O_3$  decrease.

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Sensitivity studies demonstrate that the  $O_3$  production regime in Xi'an and surrounding areas varies from  $NO_x$  to VOC-sensitive chemistry, constituting a dilemma for  $O_3$ control strategies. The industry emissions contribute the most to the  $O_3$  concentrations in Xi'an and surrounding areas, but whether individual anthropogenic emissions or bio-

- genic emissions do not play a dominant role in the  $O_3$  formation. Under the situation with high  $O_3$  and  $PM_{2.5}$  concentrations in Xi'an and surrounding areas, mitigation of  $O_3$  pollutions is challenging through decreasing emissions from various anthropogenic sources. A 50 % reduction of all the anthropogenic emissions only decreases the nearsurface  $O_3$  level by less than 14 % on average in Xi'an and surrounding areas.
  - Xi'an and surrounding areas, with more than 10 million population, are a representative region in the north of China, having experiencing rapid industrialization and urbanization in recent years. Heavy haze or photochemical smog events frequently attack the region, substantially impairing visibility and potentially causing severe health effects. Al-
- though the dispersion conditions have improved during summertime, the occurrence of heavy pollution events with both high PM<sub>2.5</sub> and O<sub>3</sub> levels is frequent in the region, exceeding China air quality standards. For the discussion convenience, we have defined two exceedance level: Level I with hourly PM<sub>2.5</sub> and O<sub>3</sub> concentrations exceeding 35 and 160 µg m<sup>-3</sup>, respectively, and Level II with hourly PM<sub>2.5</sub> and O<sub>3</sub> concentrations exceeding exceeding 75 and 200 µg m<sup>-3</sup>, respectively. We have further analyzed the real-time
- exceeding 75 and  $200 \,\mu\text{gm}^{-0}$ , respectively. We have further analyzed the real-time hourly observations of PM<sub>2.5</sub> and O<sub>3</sub> concentrations in the afternoon in mega-cities or urban complexes of the north of China, to explore the occurrence days of the defined exceedance levels during 2013 summertime (Table 2). As shown in Table 2, in Tianjin, Shijiazhuang, and Ji'nan, the occurrence days of the exceedance level II is more than



40, or haze and photochemical smog events hit the three cities simultaneously within at least 40 days in the afternoon during 2013 summertime. Thus, the model results in the present study, from an episode with high concentrations of  $O_3$  and  $PM_{2.5}$  in Xi'an and surrounding areas, can potentially provide beneficial support for the design and

- <sup>5</sup> implementation of emission control strategies in those cities in the north of China. The occurrence of high  $O_3$  levels with high  $PM_{2.5}$  concentrations constitutes a dilemma for the design of  $O_3$  control strategies. If the  $O_3$  mitigation approach decreases aerosols in the atmosphere directly or indirectly, the enhanced photolysis caused by aerosol reduction would compensate the  $O_3$  loss. If only the  $PM_{2.5}$  control strategy is implemented,
- <sup>10</sup> the O<sub>3</sub> pollution will be deteriorated. With the implementation of stringent air quality standards for  $PM_{2.5}$  in China since 2014, O<sub>3</sub> has been frequently reported to be the major pollutant during summertime in the Bejing-Tianjin-Hebei area with the decrease of the  $PM_{2.5}$  level, which is consistent with the results in the present study.

It is worth noting that, although the WRF-CHEM model exhibits good performance in simulations of the gas-phase species and aerosols compared to measurements in general, it still sometimes underestimates or overestimates the observations. One of the possible reasons for the discrepancies between simulations and observations is the uncertainty of the emission inventory, which has undergone manifest changes due to rapid urbanization and industrialization and implementation of air pollution control

- strategies in the Guanzhong basin since the base year when the emission inventory was developed, and needs further updating in future studies. The model results are also sensitive to the meteorological fields uncertainty, e.g., the biases of modeled wind fields significantly impact the simulations of the variation and pattern of the gas-phase species and aerosols in the early morning on 23 August and in the afternoon on 24 Au-
- <sup>25</sup> gust. Studies need to be conducted to further improve the meteorological field simulations in Xi'an and surrounding areas for the assessment of the O<sub>3</sub> formation.

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Predictands	Classification	MB	RMSE	IOA
Ο <sub>3</sub> (μg m <sup>-3</sup> )	Averaged	-9.0	29.	0.91
NO <sub>2</sub> (μg m <sup>-3</sup> )	Averaged	-5.2	11.	0.73
PM <sub>2.5</sub> (µg m <sup>-3</sup> )	Averaged	-1.4	21.	0.92
Temperature (°C)	Averaged	-0.76	1.1	0.97
Relative humidity (%)	Averaged	-4.5	5.5	0.92
Wind speed $(m s^{-1})$	Xi'an	1.7	2.1	0.26
	Xianyang	1.3	1.5	0.61
	Jinghe	0.14	1.1	0.74
	Lintong	1.2	1.5	0.63
	Chang'an	0.69	1.2	0.47
	Lantian	0.43	1.1	0.61

**Table 1.** Statistical comparison of simulated and measured  $O_3$ ,  $NO_2$ ,  $PM_{2.5}$ , temperature, relative humidity, and wind speed at monitoring sites from 22 to 24 August 2013.



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**Table 2.** Occurrence days of the defined  $PM_{2.5}$  and  $O_3$  exceedance levels during 2013 summertime.

	Beijing	Tianjin	Shijiazhuang	Ji'nan	Taiyuan	Xi'an
Level I <sup>a</sup>	57	65	64	72	53	61
Level II <sup>b</sup>	33	41	43	41	28	20

<sup>a</sup> hourly PM<sub>2.5</sub> and O<sub>3</sub> concentrations exceeding 35 and 160  $\mu$ g m<sup>-3</sup>, respectively <sup>b</sup> hourly PM<sub>2.5</sub> and O<sub>3</sub> concentrations exceeding 75 and 200  $\mu$ g m<sup>-3</sup>, respectively



**Figure 1. (a)** WRF-CHEM model simulation domain with topography and **(b)** geographic distributions of surface monitoring stations. In **(b)**, the blue squares represent the chemical species monitoring stations and the red circle is the IEECAS site. The red numbers denote meteorological observation sites. 1: Xi'an; 2: Xianyang; 3: Jinghe; 4: Lintong; 5: Chang'an; 6: Lantian. In addition, the area surrounded by the white rectangle in **(b)** is defined as Xi'an and surrounding areas according to the plume movement, and the area surrounded by the black line is the urban region of Xi'an.





Figure 2. Geographic distribution of emissions of (a) nitrogen oxide and (b) volatile organic compounds in the simulation domain.





**Figure 3.** Observed (black dots) and simulated (blue lines) diurnal profiles of **(a)** surface temperature and **(b)** relative humidity averaged over six meteorological sites from 22 to 24 August 2013.





**Figure 4.** Observed (black dots) and simulated (blue lines) diurnal profiles of surface wind speeds at six meteorological sites from 22 to 24 August 2013.





Figure 5. Same as Fig. 4, but for surface wind directions.





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**Figure 7.** Same as Fig. 6, but for  $NO_2$ .





**Figure 8.** Comparison of measured (black dots) and simulated (blue line) diurnal profiles of near-surface hourly (a)  $O_3$  and (b)  $NO_2$  averaged over all ambient monitoring stations from 22 to 24 August 2013.





**Figure 9. (a)** scattering plot of measured daily aerosol constituents with simulations and comparison of **(b)** measured and **(c)** modeled  $PM_{2.5}$  chemical composition (%).





Figure 10. Same as Fig. 6, but for  $PM_{2.5}$ .





Figure 11. Same as Fig. 8, but for PM<sub>2.5</sub>.





**Figure 12.** Retrieved (black dots) and calculated (blue lines) diurnal profiles of **(a)** AOD and **(b)** aerosol SSA at 440 nm at IEECAS site from 22 to 24 August 2013, and pattern comparison of calculated vs. retrieved AOD at 550 nm at 10:00 BJT **(c)** on 22 August and **(d)** 23 August 2013. Colored squares: retrieved AOD; color contour: calculated AOD.





**Figure 13.** Diurnal variations of the change of (a)  $J[NO_2]$  and (b)  $O_3$  concentrations averaged in Xi'an and surrounding areas due to aerosol effects from 22 to 24 August 2013.





**Figure 14.** Diurnal profiles of (a)  $O_3$  concentrations and (b)  $O_3$  changes averaged in Xi'an and surrounding areas caused by a 50% reduction of anthropogenic NO<sub>x</sub> and VOCs emissions, respectively, from 22 to 24 August 2013. Blue line: the reference simulation; red line: the simulation with a 50% reduction of anthropogenic NO<sub>x</sub> emissions; green line: the simulation with a 50% reduction of anthropogenic VOCs emissions.





Figure 15. Change of O<sub>3</sub> concentrations in the bottom model layer, averaged during O<sub>3</sub> peak time from 22 to 24 August 2013 due to a 50% reduction of a 50% reduction of anthropogenic (a) NO<sub>y</sub> and (b) VOCs emissions, and (c) the 3-day average ratio of  $H_2O_2/HNO_3$  during  $O_3$ peak time.

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**Figure 16.** Diurnal variations of contributions of biogenic emissions to near-surface isoprene and  $O_3$  concentrations averaged in Xi'an and surrounding areas from 22 to 24 August 2013.





**Figure 17.** Diurnal profiles of **(a)**  $O_3$  concentrations and **(b)**  $O_3$  contribution from various anthropogenic sources averaged in Xi'an and surrounding areas from 22 to 24 August 2013. Blue line: the reference simulation; brown line: the simulation without industry emissions; green line: the simulation without residential emissions; red line: the simulation without transportation emissions.





**Figure 18.** Diurnal profiles of (a)  $O_3$  concentrations and (b)  $O_3$  changes averaged in Xi'an and surrounding areas caused by a 50% reduction of various anthropogenic sources from 22 to 24 August 2013. Blue line: the reference simulation; brown line: the simulation with a 50% reduction of industry emissions; green line: the simulation with a 50% reduction of transportation emissions; the black line: the simulation with a 50% of all anthropogenic emissions.

