



Impacts of Biogenic Emissions on Summertime Ozone Formation in the Guanzhong Basin, China

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Abstract

This study is the first attempt to understand the synergistic impact of anthropogenic and biogenic emissions on summertime ozone (O_3) formation in the Guanzhong (GZ) basin where Xi'an, the oldest and the most populous city (with a population of 9 million) in the northwest China, is located. Month-long (August 2011) WRF-Chem simulations with different sensitivity experiments were conducted and compared with near-surface measurements. Biogenic volatile organic compounds (VOCs) concentrations were characterized from 6 surface sites among the Qinling Mountains, and urban air composition was measured in the Xi'an city at a tower 100 m above the surface. The WRF-Chem control experiment reasonably reproduced the magnitudes and variations of observed O_3 , VOCs, NO_x , $PM_{2.5}$ and meteorological parameters, with normalized mean biases for each parameter within $\pm 21\%$. Subsequent analysis employed the factor separation approach (FSA) to quantitatively disentangle the pure and synergistic impacts of anthropogenic and/or biogenic sources on summertime O_3 formation. The impact of anthropogenic sources alone was found to be dominant for O_3 formation. Although anthropogenic particles reduced NO_2 photolysis by up to 60%, the anthropogenic sources contributed 19.1 ppb O_3 formation on average for urban Xi'an. The abundant biogenic VOCs from the nearby forests promoted O_3 formation in urban areas by interacting with the anthropogenic NO_x . The calculated synergistic contribution (from both biogenic and anthropogenic sources) was up to 14.4 ppb in urban Xi'an, peaking in the afternoon. Our study reveals that the synergistic impact of individual source contributions to O_3 formation should be considered in the formation of air pollution control strategies, especially for big cities in the vicinity of forests.

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Keywords: ozone, emission, biogenic volatile organic compounds, WRF-Chem



1. Introduction

Elevated ozone (O_3) levels in China has drawn increasing attention in recent years (e.g. Xue et al., 2014; Hu et al., 2016; Wang T. et al., 2016; Wang M. et al., 2016). O_3 , a secondary pollutant, is mainly formed by complex photochemical reactions of nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs). High O_3 concentration at ground level is harmful to human health and ecosystems (WHO, 2005; Feng et al., 2015; Brauer et al., 2016). O_3 in the troposphere is an important greenhouse gas that has the third-highest radiative forcing after CO_2 and CH_4 (Stevenson et al., 2013; IPCC, 2013). In addition, O_3 is the primary source of the hydroxyl radical (OH), which has a major influence on the oxidizing capacity of the atmosphere and thus impacts the oxidation chemistry of secondary pollutants (e.g. sulfate and secondary organic aerosol) (Ehhalt et al., 2000; Rohrer et al., 2006). In recent years, the surface O_3 level has been increasing in most Chinese cities. For instance, in the highly urbanized areas in China, maximum 8h O_3 concentration increased by 98% (22 ppb) from 2013 to 2017 in the Yangtze River Delta (YRD) region, and the growth trend was 41% (13 ppb) for Beijing-Tianji-Hebei (BTH) region and 30% (10 ppb) for the Pearl River Delta (PRD) region (<http://datacenter.mep.gov.cn>). In the future, the pollution trend is likely to worsen due to potential changes of climate and emissions (Wang et al., 2013; Liu et al., 2013; Zhu et al., 2016, 2017).

On the global scale, VOC emissions from natural vegetation is estimated to be one order greater than that from anthropogenic activities, in spite of large uncertainties in different studies (Guenther et al., 2006; Wu et al., 2007, 2008; Jiang et al., 2013; Zhu et al., 2017). In addition, biogenic VOCs (e.g. isoprene) are highly reactive, reacting more efficiently with OH than most anthropogenic VOC species (Carlo et al., 2004). Previous studies have demonstrated the significant impacts of biogenic VOCs on surface O_3 formation under strong solar radiation, high temperature and NO_x level (e.g. Fiore et al., 2005, 2011; Wang et al., 2008; Curci et al., 2009; Geng et al., 2011; Strong et al., 2013; Squire et al., 2014; Lee et al., 2014; Zhang et al., 2017). In China, biogenic VOC emissions are estimated to be 17-44 TgC yr^{-1} (Guenther et al., 1995; Lin et al., 2008; Fu et al., 2012, 2104; Li et al., 2014), and are concentrated in the warm summer season. Current studies report that biogenic VOCs contribute to surface O_3 concentrations in China (Geng et al., 2011; Qu et al.,



2013, 2014) and play an important role in intercontinental transport of O₃ (Zhu et al., 2017).

The impacts of biogenic VOCs on O₃ formation may vary in different regions and different seasons (Im et al., 2011; Strong et al., 2013; Wagner et al., 2014; Lee et al., 2014). Qu et al. (2013) employed the RAQM model to examine the influence of biogenic emissions on daily maximum surface O₃ concentration in China. Their calculations showed that in general the impact from biogenic sources on O₃ were more obvious in South China than in North China, but the O₃ increments in different regions didn't follow the same seasonality. Geng et al. (2011) used the WRF-Chem model to evaluate the effect of biogenic emissions on O₃ production in Shanghai in summer, and suggested that the carbonyls produced by the continuous oxidation of isoprene have important impacts on O₃ level in the city. In addition, some studies suggest that biogenic emissions may increase due to global warming and land-use change, and the impact on O₃ formation could be more significant in the future (Lin et al., 2008; Fiore et al., 2011; Liu et al., 2013; Fu et al.; 2015). Fiore et al. (2011) pointed out that the potential increases in biogenic isoprene in North American (NA) could offset the regional and intercontinental surface O₃ decreases produced by controls on NA anthropogenic emissions during warm seasons.

The Guanzhong (GZ) basin is the most developed region in northwestern China. In the past few years, air pollution has grown up to be a severe issue in the GZ basin (Wang et al., 2012; Xue et al., 2017), due to its specific basin topography and abundant anthropogenic emissions (Li et al., 2017). According to the data from national environmental monitoring stations in the GZ basin, 43% of days in 2013-2017 have AQI > 100 (e.g., unhealthy air quality category), and in summer O₃ was regarded as the primary pollutant in 70% of polluted cases. In this study, we employed a regional chemical model WRF-Chem to simulate O₃ concentration in the GZ basin for summer 2011. Our aim is the source apportionment of urban O₃ formation in this city surrounded by forests, specifically quantifying the individual and synergistic contributions of anthropogenic and biogenic sources. The paper is organized as follows. We first describe the sampling campaign, the chemical model and the emission data used for driving the model (Section 2). We then evaluate the model performance by comparing the observed urban air quality and biogenic VOCs



with the simulated results (Section 3). Finally, we analyze the sensitivity of summertime O₃ formation to biogenic and anthropogenic sources (Section 4).

2. Methodology

5 2.1 Sampling sites and descriptions

The study was conducted in Xi'an, one of the oldest cities in the world. Xi'an is the most populous city in the northwest of China with a population of greater than 9 million. It is located in the heartland of the GZ basin between the Qinling Mountains and the Loess Plateau (Fig. 1). The topographical features result in air pollutants often being trapped in the valley with limited dispersion. The city borders the northern foot of the Qinling Mountains, only around 50 kilometers from downtown to the foothills. The Qinling Mountains are an east-west mountain range of 1600 kilometers in length and 300 kilometers in width and are regarded as a natural boundary between Northern and Southern China. Climate, and even culture are significantly different from the north to the south. The Xi'an city has high temperatures and strong solar intensity in summer, making it an ideal location to assess the importance of biogenic contributions to urban air quality.

2.1.1 Biogenic VOC measurements in the Qinling Mountains

We collected ambient air samples at six field sites in the Qinling Mountains (Fig. 1b, the triangles) on 6th – 7th August 2011 under sunny weather conditions (details are presented in Table 1). Sampling was conducted between 9:30 am to 16:30 pm local time to target expected daily maximum isoprene concentrations. At each site, ambient air samples were pulled in parallel onto three cartridges filled with Tenax GR and Carbograph 5TD solid adsorbents using a mass flow controlled pump for 30 min. Samples were shipped to the lab at NCAR (Boulder CO, USA) for chemical analysis. Cartridges were desorbed using an UltraTM TD auto sampler with a Unity thermal desorption system (MARKES International Series 2, Llantrisant, UK) interfaced with a temperature programmed Agilent 7890A series Gas Chromatograph with a 5975C Electron Impact Mass Spectrometer and a Flame Ionization Detector (GC-MS/FID, Agilent Technologies, Santa Clara, CA, USA). We used nitrogen as a carrier gas at the flow rate of 3 mL min⁻¹. Isoprene and monoterpene identifications were based on



the comparison of retention time of authentic standards and mass spectra in the National Institute of Standards and Technologies (NIST) databases. Quantifications were calculated using FID calibrated with a NIST traceable standard.

2.1.2 Air quality monitoring in urban Xi'an

5 We set up an urban air quality monitoring site (Fig. 1b) at the roof (107 m above ground) of the main building (108.984 °E, 34.245 °N) on the campus of Xi'an Jiaotong University to minimize the ground level influences of local emissions. The campus is in the southeastern part of the downtown surrounded by residential areas. We obtained reliable observations of the concentrations of O₃, NO_x and PM_{2.5} during 15th – 30th
10 August 2011. Gases were measured by Ecotech analyzers (Ecotech Pty Ltd, Australia). O₃ were measured by an UV photometric analyzer EC9801. NO_x was measured by a gas-phase chemiluminescence detection analyzer EC9841. We collected 24h PM_{2.5} filter samples by a mini-volume sampler (Airmetrics, USA) at a flow rate of 5 L min⁻¹ using both 47 mm quartz-fiber (Whatman, Mid-dlesex, UK) and teflon-membrane
15 (Gelman, Ann Arbor, MI) filters. We calculated the PM_{2.5} mass concentrations gravimetrically by weighing the teflon-membrane filters pre and post-collection for at least 4 times using an electronic microbalance (MC5, Sartorius, Göttingen, Germany) with ±1 µg sensitivity under controlled conditions. EC and OC concentrations were analyzed based on a 0.5 cm² punch from the quartz-fiber filter following the
20 IMPROVE_A (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow et al., 2007) using a DRI model 2001 Carbon Analyzer. The concentrations of ions were quantified from a 10.8 cm² of the teflon-membrane filter by a Dionex DX-600 ion chromatography (Dionex Inc., Sunnyvale, CA, USA) (Zhang et al., 2014).

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2.2 The WRF-Chem model

We employed the WRF-Chem model to study biogenic VOC emissions from the Qinling Mountains and their contributions to regional O₃ formation in urban Xi'an. WRF-Chem is a 3-D online-coupled meteorology and chemistry model consisting of
30 the components of emission, transport, chemical transformation, photolysis and radiation (Tie et al., 2003, Li et al., 2011), dry and wet deposition (Wesely, 1989), and aerosol interactions (replaced with CMAQ aerosol module, Binkowski and Roselle,



2003; Li et al., 2010). WRF is a non-hydrostatic mesoscale dynamical system with various options for physical parameterizations (Skamarock et al., 2008). The chemical modules were implemented into the WRF framework obeying the same schemes for the simultaneous simulations (Grell et al., 2005).

5 We adopted RADM2 (Regional Acid Deposition Model) as the gas phase chemical mechanism to predict O₃ formation. RADM2 is an aggregated species type using the reactivity based weighting scheme to adjust for lumping (Stockwell et al., 1990). The mechanism implemented in our WRF-Chem model covers 158 reactions among 36 species, containing the complete reaction paths for isoprene, monoterpenes
10 and the relevant inorganic reactions. As an explicit species, isoprene chemistry is based on an updated CB4 gas-phase mechanism (Carter and Atkinson., 1996). Monoterpenes are represented by a unique species TERP, with the reactions of OH, O₃, and NO₃. These reactions use the same rate constants as the reaction of OLI (Internal olefins), and have the TERPAER counter species added to track the
15 throughput of this reaction.

The simulated domain (Fig. 1) is 600×600 km² centered on urban Xi'an with 3 km horizontal grid spacing. We set up 28 vertical layers from the surface up to 50 hPa with 7 layers below 1 km to assure a high near-ground vertical resolution. The National Centers for Environmental Prediction (NCEP) FNL Operational Global
20 Analysis data provided the initial and boundary fields of meteorology. Initial and boundary conditions of chemistry were derived by a global chemical transport model (Model for Ozone and Related chemical Tracers, MOZART) (Emmons et al., 2010). We considered the first 7 days as spin-up period, and the study focused on 6th – 7th and 15th – 30th August 2011 because of the available field observation datasets (as
25 described in Section 2.1).

2.3 Biogenic and anthropogenic emissions

Biogenic emissions were quantified by the widely used model MEGAN (Model of Emissions of Gas and Aerosols from Nature) (Guenther et al., 2006). MEGAN
30 coupled into the WRF-Chem model, referred to here as WRF-MEGAN2, provides on-line estimates of the net landscape-averaged biogenic emissions from terrestrial ecosystems into the above-canopy atmosphere. The on-line estimated emissions of



isoprene, individual monoterpenes and other biogenic VOCs serve as the inputs for the further chemistry simulation. To drive MEGAN, we need the following inputs: emission factors (EFs), leaf area index (LAI), plant functional types (PFTs), as well as meteorology conditions. The meteorology was obtained from WRF simulations and the LAI and PFT data were extracted from MODIS (Tian et al., 2004). We adopted
5 the canopy-scale emission factors of dominant species from Guenther et al. (2006).

Estimated the whole year 2011 by WRF-MEGAN2, the isoprene and monoterpene emissions in the Qinling Mountains were mostly concentrated in summer (71% and 58%, respectively). During our simulation period, the isoprene emission from the domain is 157 Gg mon^{-1} , accounting for ~80% of total biogenic VOC emissions
10 (Table 2). The rest are monoterpenes and other biogenic VOCs (e.g. acetone and MBO (2-methyl-3-buten-2-ol)). Figures 2a and 2b show the spatial distributions of biogenic isoprene and monoterpenes emission fluxes during the simulation period, indicating the high emission zone of isoprene in the Qinling Mountains lying to the
15 south of the Xi'an city.

The anthropogenic emissions were obtained from the Multi-resolution Emission Inventory for China (MEIC, Li et al., 2017) for the year of 2010, which was downscaled to a resolution of 3 km using locations of point sources and various spatial proxies (Geng et al., 2017). The upgraded highly resolved emission data were
20 based on a collection of statistics and newly developed emission factors. The emission inventory used in our model includes all major anthropogenic sources, but excluded open biomass burning which occupies a low proportion in the GZ basin during our simulating period (estimated by Fire Inventory from NCAR, <https://www2.acom.ucar.edu/modeling/finn-fire-inventory-ncar>). The anthropogenic
25 emission sources are composed of power, industry, residential, transportation, and agriculture. The inventory of VOCs, SO_2 , NO_x , NH_3 , and $\text{PM}_{2.5}$ in the domain during the simulation period is summarized in Table 2. The estimated anthropogenic VOCs emissions are 72.2 Gg, contributing up to ~30% of total VOC emissions. Figures 2c and 2d present the spatial distributions of anthropogenic VOC and NO_x emissions in
30 the simulation period. The highest emission intensity of anthropogenic VOCs and NO_x are in Xi'an city and the GZ basin due to the frequent vehicle and industrial activities of this area.



2.4 Factor Separation Technique

O₃ is formed by complicated nonlinear reactions of anthropogenic and biogenic precursors (NO_x and VOCs) in the presence of sunlight. The approach referred to as the “brute-force” method is traditionally used in air quality model to identify source contributions from specific non-reactive species in a linear process, but it is not straightforward to quantify the contributions of several different factors in a nonlinear process. In practice, the actual impact of one factor in a nonlinear process in the presence of others can be separated into 1) pure impact from the factor and 2) interactional impacts from all those factors. In this study, we adopted the factor separation approach (FSA) (Stein and Alpert, 1993) to decompose the pure contribution of a factor from its interaction with other factors.

We considered anthropogenic and biogenic sources as two interactional factors to influence the O₃ formation. $f_{anth-bio}$, f_{anth} , f_{bio} and f_0 are the simulation results including both anthropogenic and biogenic sources, anthropogenic source only, biogenic source only, and neither, respectively. Pure contributions of anthropogenic and biogenic sources are expressed as Eq. (1) and (2), respectively:

$$f'_{anth} = f_{anth} - f_0 \quad (1)$$

$$f'_{bio} = f_{bio} - f_0 \quad (2)$$

The calculated result including both anthropogenic and biogenic sources should include both pure contributions of the two factors, the synergistic impact, and the impact of background transport (Eq. 3):

$$f_{anth-bio} = f'_{anth} + f'_{bio} + f'_{anth-bio} + f_0 \quad (3)$$

Thus, the synergistic effect between anthropogenic and biogenic sources is represented as:

$$\begin{aligned} f'_{anth-bio} &= f_{anth-bio} - f'_{anth} - f'_{bio} - f_0 \\ &= f_{anth-bio} - (f_{anth} - f_0) - (f_{bio} - f_0) - f_0 \\ &= f_{anth-bio} - f_{anth} - f_{bio} + f_0 \end{aligned} \quad (4)$$

Based on the FSA, we conducted four simulations, namely BASE, ANTH, BIO and NEITHER, to explore the pure and synergistic impacts of anthropogenic and/or



biogenic sources on O₃ production in the GZ basin. Detailed simulation settings and the various contribution definitions are summarized in Table 3.

3. Observation data and model validation

5 3.1 Meteorology

The specific topographical features of Xi'an make the meteorological conditions crucial for the accumulation and dispersion of urban pollutants. To validate our model performance in wind, temperature and relative humidity, we compared the hourly meteorological data (<http://www.meteomanz.com>) observed at the Jinghe site
10 (108.58 E, 34.26 N, in the west of Xi'an) with model simulations. Figure 3c illustrates the observed and simulated near-surface wind speed and directions during 15th – 30th August 2011. The WRF-Chem model successfully captured the prevailing wind direction from north and northeast, consistent with the in-situ observations. It should be noted that in our simulation period the prevailing wind blew from south,
15 which enhanced the transport of biogenic emissions from the Qinling Mountains to urban Xi'an. In addition, a continuous rainfall event during 18th-22nd August (green shadow in Fig. 3) was characterized by lower temperature and near-saturated humidity.

We conducted the statistical verification of meteorological variables in Table 4,
20 including the *r* (correlation coefficient), NMB (normalized mean bias) and RMSE (root mean square errors). Modeled meteorological variables were in good agreement with observations (Fig. 3a-c) with the NMB less than ±6%.

3.2 Biogenic VOC concentrations in the Qinling Mountains

25 Samples from the Qinling Mountains show that the dominant VOC species was isoprene, and α-pinene was the main constituent of monoterpenes (Table 1). The ratio of isoprene to monoterpenes varies considerably. We compared the VOC measurements with model simulations to validate whether the calculated results were reasonable. The isoprene mean concentration simulated in the six grids was 1.4 ppb,
30 which is close to the observed average value of 1.3 ppb at the six sampling sites.



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Monoterpenes performed quite similarly, simulated 0.22 ppb comparing with observed 0.21 ppb. The evaluation indicates that biogenic VOCs simulations reasonably agreed with the observations in the Qinling Mountains, on average, which provides a basis for us to further evaluate biogenic effects on O₃.

3.3 Gaseous and particulate pollutants in urban Xi'an

The sampling campaign was organized in summer. Based on the gaseous and particulate pollutant observations, the daily mean PM_{2.5} concentration was 90.0±53.5 μg m⁻³, with 57% of days exceeding the WHO Interim target-1 (IT-1) 75 μg m⁻³. The daily mean NO_x concentrations were 25.8-63.2 ppb, with 40% of days exceeding the guideline 48.7 ppb (≈100 μg m⁻³, GB 3095-2012). The maximum 8h O₃ concentration was 3.5-95.6 ppb, with most of the values around the national first grade standard of 46.6 ppb (≈100 μg m⁻³, GB 3095-2012). Summer in Xi'an is monitored as the least polluted season of the year, and the case we picked is regarded as a typical situation in summer Xi'an.

Figure 3 compares the simulated hourly O₃ and NO_x concentrations with in-situ observations. During the rainy episode (the green shadow in Fig. 3), our model overestimated NO_x concentration and underestimated O₃ concentration. The deviation can be explained by the failure to simulate the precipitation in the WRF model resulting in underestimates in wet deposition. So, we focused our analysis on the period excluding the rainy period. During the no-raining days, our model well reproduced the diurnal variations and magnitudes of O₃ and NO_x concentrations. The simulated hourly NO_x averaged for the no-raining period was 46.6 ppb, close to the observed 47.0 ppb (NMB=-1%). For O₃, the calculated result averaged for no-raining period was 38.7 ppb, ~20% higher than the observed value of 31.5 ppb. Our simulated O₃ also reproduced the temporal variation of the observed O₃ (r = 0.72).

We analyzed PM_{2.5} concentration and composition (sulfate, nitrate, ammonium, EC, organic matter) with the filter-base measurements. The simulated PM_{2.5} concentration was 94.6±28.2 μg/m³, slightly lower (NMB=-12%) than measured 107 μg/m³ averaged for the no-raining period. The simulated results agreed well with observed PM_{2.5} compositions (Fig. 4b and 4c). Sulfate is the dominant constituent of both simulated (32%) and observed (37%) PM_{2.5}. High sulfate concentration was



mainly attributed to the high SO₂ emission in the GZ basin as well as the humid weather conditions (Wang et al., 2014). The secondary constituent of observed PM_{2.5} is organic matter, which accounted for 16% of the total observed PM_{2.5}, close to the simulated result (14%). Secondary organic matter contributed half to total simulated
5 organic matter, mainly due to the abundant precursor (i.e. VOCs) emissions and the high atmospheric oxidation capacity in summer.

4. Impacts of anthropogenic and biogenic sources on O₃ formation

In this section, we analyzed the results from the four simulations (BASE, ANTH,
10 BIO and NEITHER, Table 3) to characterize the fate of O₃ and its precursors in the GZ basin and to quantify the pure and synergistic impacts of anthropogenic and/or biogenic sources on summertime O₃ formation.

4.1 Base simulation of O₃

Firstly, we discussed the spatial and temporal characteristics of the simulated O₃
15 and the precursors (VOCs and NO_x) in the GZ basin in the BASE simulation.

Figure 5a shows spatial distribution of the simulated VOCs during the no-raining period, overlaid with the simulated wind vectors. The highest concentration (more than 50 ppb) was in urban Xi'an and its downwind region (the southwest of urban Xi'an), due to anthropogenic activities. In addition, another high-value area (~30 ppb)
20 was found in the Qinling Mountains, which was probably due to biogenic sources. To better understand the composition of VOCs, we analyzed some typical individual VOC species. Figure S1a shows the spatial distribution of xylenes, representing anthropogenic VOCs, and Fig. S2a and S3a show isoprene and monoterpenes, representing biogenic VOCs. The anthropogenic xylenes were mainly distributed in
25 the GZ basin, while the high biogenic isoprene and monoterpene concentrations were found over the Qinling Mountains. These results explain the spatial feature of total VOCs and the dominant sources. Detailed discussion of source apportionment is given in Section 4.2

The spatial distribution of NO_x was slightly different (Fig. 6a). The highest
30 concentrations of NO_x were in the GZ basin (average of 11.1 ppb), especially in urban



Xi'an (averaged of 30.1 ppb), while among the Qinling Mountains, NO_x was low and dominated by biogenic sources.

PM, even though not directly involved in the formation pathways of O_3 , influences the chemical equilibrium indirectly. In the daytime, NO_2 photolysis frequency ($J(\text{NO}_2)$) is determined by the solar radiation influenced by PM via scattering and absorption. Figure 7 shows the changes of $J(\text{NO}_2)$ under the participation of PM averaged for urban Xi'an. $J(\text{NO}_2)$ was reduced by 40-60%, most significantly in morning and evening rush hours. In the night time, $\text{PM}_{2.5}$ can remove N_2O_5 from the NO_x cycle via heterogeneous reactions, as one of the major NO_x sinks in the atmosphere (Xue et al., 2014). Figure 8a shows the spatial feature of $\text{PM}_{2.5}$. The densest area was urban Xi'an (averaged for $102 \mu\text{g m}^{-3}$) followed by the western part of the GZ basin. The spatial distribution of high-values of $\text{PM}_{2.5}$ was similar to that of NO_x , but covered a wider area mostly in the downwind region of urban Xi'an, which is expected due to the time required for secondary aerosol formation and thus further dispersion.

The typical diurnal variation of O_3 (Fig. 9b) demonstrates there are higher concentrations in the afternoon and lower at night. For better understanding of O_3 concentration characteristics and source/sink mechanisms, we discussed two different time scales: 1) O_3 peak time (14:00-18:00) (Fig. 10) and 2) O_3 24-hour average (Fig. 11). During the peak time, simulated near-surface O_3 was high in the GZ basin, with averaged concentration of 75 ppb. In the downwind region of high NO_x and VOCs in the west of urban Xi'an, the concentration reached up to 110 ppb. We employed the ratio of $\text{H}_2\text{O}_2/\text{HNO}_3$ to investigate the chemistry regime of O_3 formation (Sillman 1995; Wang et al., 2017). If the ratio is greater than 0.5, the O_3 production regime is considered NO_x -controlled, otherwise VOC-controlled if the ratio less than 0.3. The range between 0.3 and 0.5 is defined as the transition regime from NO_x - to VOC-controlled, indicating the competition of both NO_x and VOCs in O_3 production. Figure 12a shows the spatial distribution of the simulated $\text{H}_2\text{O}_2/\text{HNO}_3$ ratio during the O_3 peak time. The urban Xi'an and the west and southeast of the GZ basin were right in the transition regime with a complicated O_3 production mechanism sensitive to both NO_x and VOCs. Most of the rest of the simulation region was VOC-controlled, excluding the Yuncheng and Hejing cities in the neighboring Shanxi provinces.



On the 24h average scale, the spatial distribution of O₃ presented a different picture (Fig. 11). The original high-value area during the peak time in the GZ city cluster shifted to low-value region due to the consumption of O₃ by abundant NO_x emissions. At night time, the titration effect of freshly emitted NO dominates, and the O₃ concentration tends to drop to a lower level. The high value of 24h averaged O₃ converged in the south and northwest outside of the GZ Basin. Those areas have elevated O₃ due to high daytime production, similar to the nearby zone of peak O₃, but also have lower emissions of NO resulting in lower loss of O₃.

4.2 Pure impact of anthropogenic or biogenic sources

Using the FSA method, we evaluated the pure contribution of anthropogenic or biogenic sources to the summertime O₃ formation in the GZ basin. In the scenario of pure contribution of anthropogenic emissions, the VOC concentrations were mostly distributed over the GZ city cluster (8.0 ppb), especially in urban Xi'an (26.4 ppb) (Fig. 5c). In the scenario of pure contribution of biogenic emissions, the VOCs were widely dispersed over the Qinling Mountains (Fig. 5d), with a calculated 9.9 ppb for the GZ basin and 12.4 ppb for urban Xi'an. NO_x concentration has the similar pattern as VOCs in the scenario of pure contribution of anthropogenic emissions, with averaged concentrations of 11.0 ppb for the GZ basin and 30.3 ppb for urban Xi'an (Fig. 6c). However, in the GZ basin and urban Xi'an, biogenic sources contributed less than 0.2 ppb to NO_x concentration (Fig. 6d). In the scenario of pure contribution of anthropogenic emissions, was PM_{2.5} spread over a wider area (Fig. 8c), due to the time required for secondary aerosol formation. In the scenario of pure contribution of biogenic emissions, PM_{2.5} was mostly distributed among the Qinling Mountains (Fig. 8d), but the concentration was lower by one order of magnitude (Table 5, Fig. S4).

In the scenario of pure contribution of anthropogenic emissions, daily peak O₃ accumulated in the downwind region in the center and western GZ due to high VOCs and NO_x concentrations. Daily peak O₃ concentrations reached 22.6 ppb for GZ and 19.1 ppb for urban Xi'an (Fig. 10c). Lower daily peak O₃ concentration was found outside of GZ basin where less anthropogenic VOCs and NO_x was emitted. In contrast, daily peak O₃ was negligible (less than 3 ppb) in the scenario of pure contribution of biogenic emissions (Fig. 10d) due to the low NO_x emissions. However, the



distribution of 24h averaged O₃ was different from daily peak O₃. 24h averaged O₃ concentration in the scenario of pure contribution of anthropogenic emissions was more diluted in the GZ city cluster than for surrounding areas (Fig. 11c). Due to the abundant NO emission and its titration effect on O₃, the pure effect of anthropogenic sources was negative, calculated to be -2.2 ppb in urban Xi'an.

4.3 Synergistic impact of the interaction between anthropogenic and biogenic sources

The synergistic impact on O₃ formation includes the interactions between anthropogenic and biogenic sources. In other word, it reflects the potential production trend of either “O₃-promoted” or “O₃-suppressed” under the natural coexistence of all emission sources. In the cases of NO_x, VOCs and PM_{2.5}, the synergistic impacts contributed less than ±3% of total concentrations (Fig. 5b, 6b, 8b, S4, and Table 5). However, the synergistic impact on O₃ played a remarkable role showing positive impacts for both daily peak (Fig. 10b) and 24h averaged O₃ (Fig. 11b). It means that the mixed state of anthropogenic and biogenic sources potentially enhanced the O₃ production more than each single source. To make it more specific, we assumed the original state was the result from ANTH simulation without the biogenic sources (Table 3). Figure 12b shows the original state O₃ production regime in the simulated region. VOC-controlled O₃ production regime covered the west of urban Xi'an and the southeast of the GZ basin. In the rest of the GZ basin and the neighboring Shanxi provinces, the O₃ production was in the transition regime, controlled by both NO_x and VOC. NO_x-controlled O₃ production regime dominated the rest of the region. After we included biogenic VOC emissions in the simulation, the O₃ concentration was significantly enhanced in the VOC-controlled regions, and partly enhanced in the mix-controlled region. However, in the VOC-controlled region, the synergistic impact contributed little.

The synergistic impact is of great importance, approximately the same magnitude as the impact from pure contributions of anthropogenic sources. The synergistic impact contributed daily peak O₃ concentrations of 10.5 ppb for the GZ basin and 14.3 ppb for urban Xi'an, while the pure anthropogenic impact contributed 22.6 ppb for GZ basin and 19.1 ppb for urban Xi'an. However, the extent was ~50% smaller on



the 24h averaged scale, but still increased O₃ concentration by 5.8 ppb for the GZ basin and 6.8 ppb for urban Xi'an. Figure 9 shows the diurnal variation of the observed and simulated O₃ concentration at Xi'an Jiaotong University, as well as the tested contributing components. Transport dominated O₃, constantly contributing
5 30-40 ppb as background. The impact of pure anthropogenic sources was positive on O₃ production during 13:00-19:00 but negative during the rest of the time, and the impact of pure biogenic sources was negligible. Synergistic impact of both anthropogenic and biogenic sources resulted in a positive contribution during 10:00-21:00, comparable to the impact of pure anthropogenic sources.

10 We evaluated the actual contributions from anthropogenic or biogenic sources. The actual contribution is defined as the combination with both pure and synergistic contributions. Actual contribution from anthropogenic sources to NO_x in urban Xi'an was 29.6 ppb, accounting 98% of total NO_x. Similarly, actual contribution from anthropogenic sources to PM_{2.5} was 91.1 μg m⁻³, comprising 89% of total PM_{2.5}. In
15 term of VOCs, the actual impact of the anthropogenic source contributed 26.2 ppb (58%), while the biogenic source contributed 12.2 ppb (27%). Due to the synergistic impact on peak O₃, both the actual effect of anthropogenic (33.4 ppb) and biogenic (16.8 ppb) sources were noticeable.

20 5. Conclusions and discussion

The GZ basin is a representative region in the northwest of China, suffering serious air pollution in recent years. Geographically, the GZ basin borders the northern foot of the Qinling Mountains. For this reason, in addition to the anthropogenic emissions from metropolitan areas, biogenic emissions are of great
25 importance in the region, especially in warm season with active photochemistry. In this study, we used the WRF-Chem model to simulate O₃ in the GZ basin and compared the results to near-surface measurements, with the aim of quantifying the pure and synergistic impacts of anthropogenic and/or biogenic sources on summertime O₃ formation. The simulation was driven by the best currently available
30 inventory of anthropogenic emissions and online calculated biogenic emissions. Near-surface measurements were captured from 6 surface sites among the Qinling



Mountains for biogenic VOCs and one 100-m-high site in the Xi'an city for air quality (NO_x , VOCs, O_3 and $\text{PM}_{2.5}$).

Our model successfully reproduced the observed air quality and meteorological parameters. The biogenic VOCs simulation showed a reasonable agreement. Our
5 model also well-reproduced the magnitudes and variations of O_3 , NO_x and $\text{PM}_{2.5}$ concentrations excluding rainy days, with normalized mean bias less than $\pm 21\%$.

We further conducted three scenario simulations to explore the pure and synergistic impacts of anthropogenic and/or biogenic sources on O_3 and the precursors, by using the factor separation approach (FSA). The results concluded that, for the
10 precursors, pure impact of anthropogenic source contributed 99% of NO_x , 80% of $\text{PM}_{2.5}$, and 33% of VOCs in the GZ basin, and pure impact of biogenic source contributed 40% of VOCs but only 1-5% of $\text{PM}_{2.5}$ and NO_x . Meanwhile, synergistic impacts from the combination of anthropogenic and biogenic sources did not bring significant changes on NO_x , VOCs and $\text{PM}_{2.5}$ (less than $\pm 4\%$). In the case of daily
15 peak O_3 , the pure impact of anthropogenic source remained the dominant contributor (19.1 ppb for urban Xi'an), even after anthropogenic particles reduced the NO_2 photolysis by up to 60%. The abundant biogenic VOCs from the nearby forests promoted the O_3 formation by interaction with anthropogenic NO_x , contributing 14.4 ppb to O_3 in urban Xi'an. This synergistic impact presented a positive contribution to
20 O_3 production throughout the day and the positive effect was much more prominent during 12:00-19:00.

O_3 pollution in China has been raising increasing concerns in recent years. Some scientists hold the view that excessive concentration of $\text{PM}_{2.5}$ suppressed the
25 formation of O_3 in the past, hiding the problem temporally. However, with the effective control of $\text{PM}_{2.5}$, O_3 pollution is manifested. The phenomenon can also be demonstrated by the government control action during G20 summit (The Group of Twenty Finance Ministers and Central Bank Governors) in Hangzhou in 2016. The concentration of $\text{PM}_{2.5}$ was depressed sharply under the strict emission control, but O_3 concentration was even higher than usual. Better understanding of O_3 pollution
30 sources/sinks and formation mechanisms in high $\text{PM}_{2.5}$ exposed area in China will benefit and guide the implementation of $\text{PM}_{2.5}/\text{O}_3$ cooperative control. Our results suggest that, in big cities geographically close to forest, O_3 pollution can be enhanced



by the synergistic impact from the combination of biogenic and anthropogenic sources. The synergistic contribution of each single source to O₃ formation cannot be neglected when making pollution control strategies.

5

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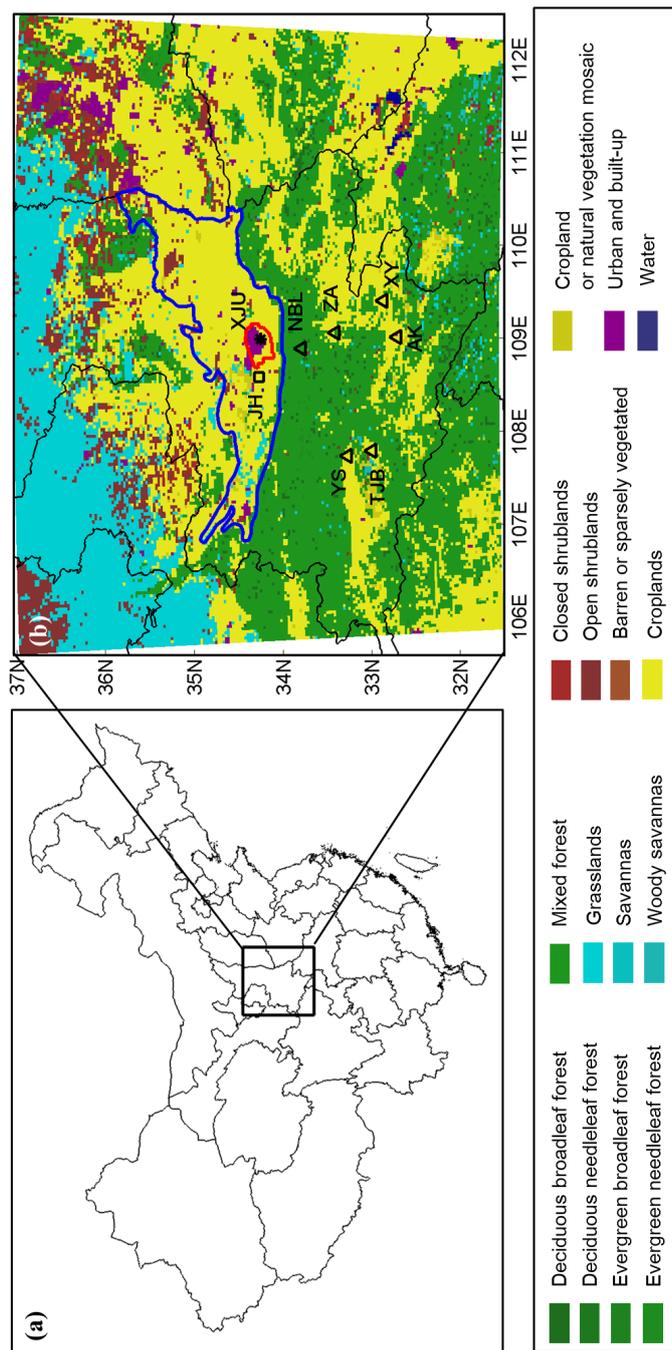


Figure 1. The simulation domain and the locations of six biogenic VOCs sites (triangles), one meteorological site (square) and one air quality site (snowflake). Underlain are land types from MODIS. The area of red line indicates the urban area of the Xi'an city. The area of blue line indicates the GZ basin.

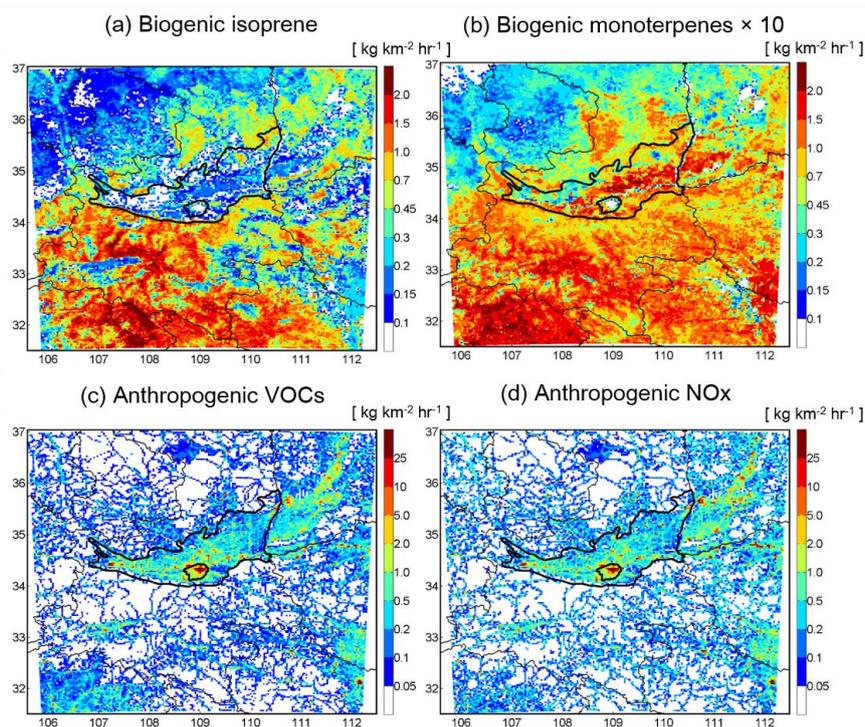


Figure 2. Monthly mean emissions of (a) biogenic isoprene, (b) biogenic monoterpenes, (c) anthropogenic VOCs and (d) anthropogenic NO_x in the GZ basin and surrounding areas in August 2011.

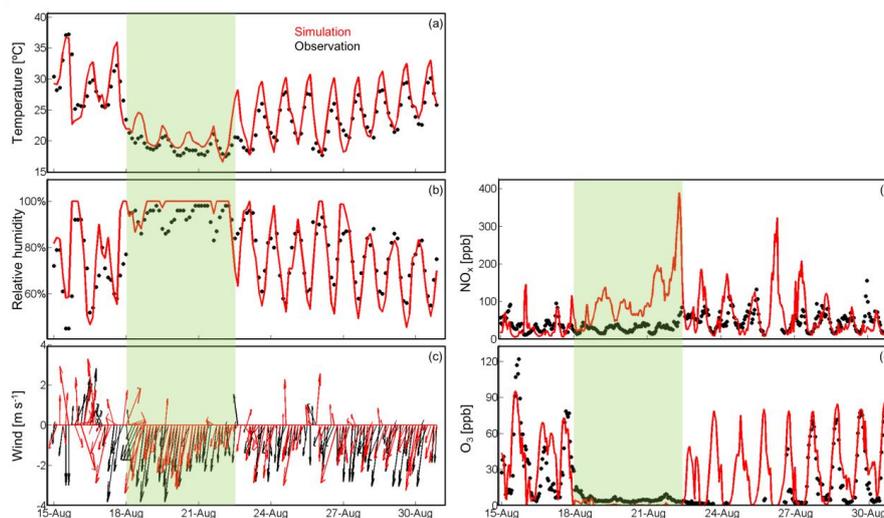


Figure 3. Observed (black) and simulated (red) temporal patterns of temperature (a), relative humidity (b) and wind (c) at the Jinghe site and NO_x (d) and O_3 (e) concentrations at Xi'an Jiaotong University during the period from 15th to 30th August 2011. The green shadow (18th -22nd August) indicates rainy days.

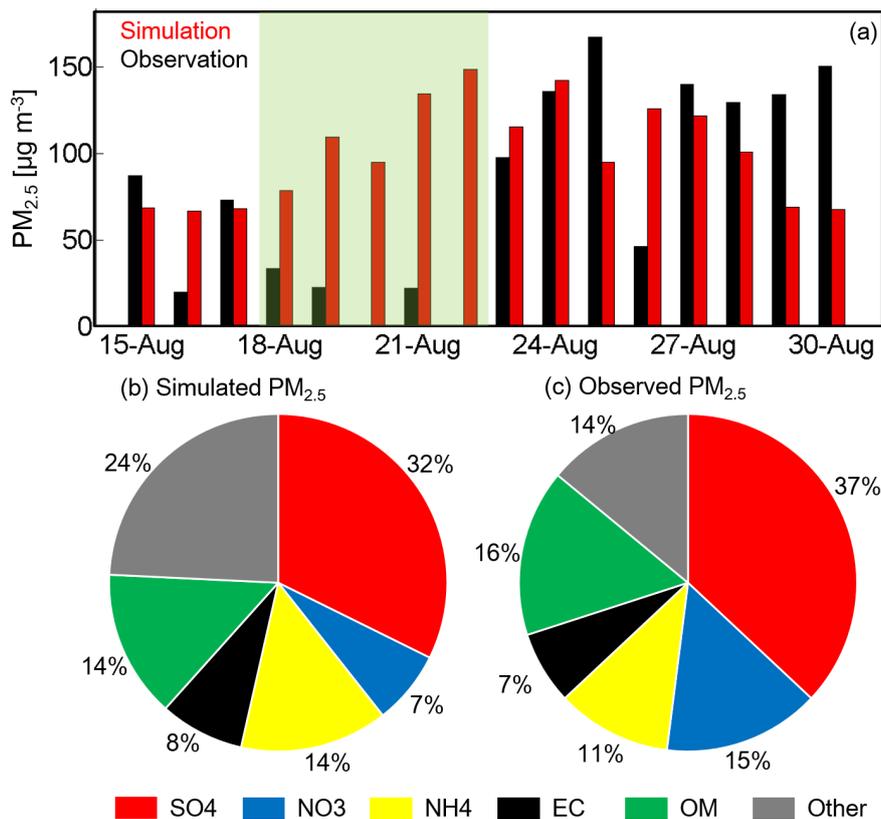


Figure 4. Observed and simulated PM_{2.5} concentrations (a) and compositions (b and c) at Xi'an Jiaotong University in August 2011. The components are calculated during the periods excluding the rainy days (the green shadow).

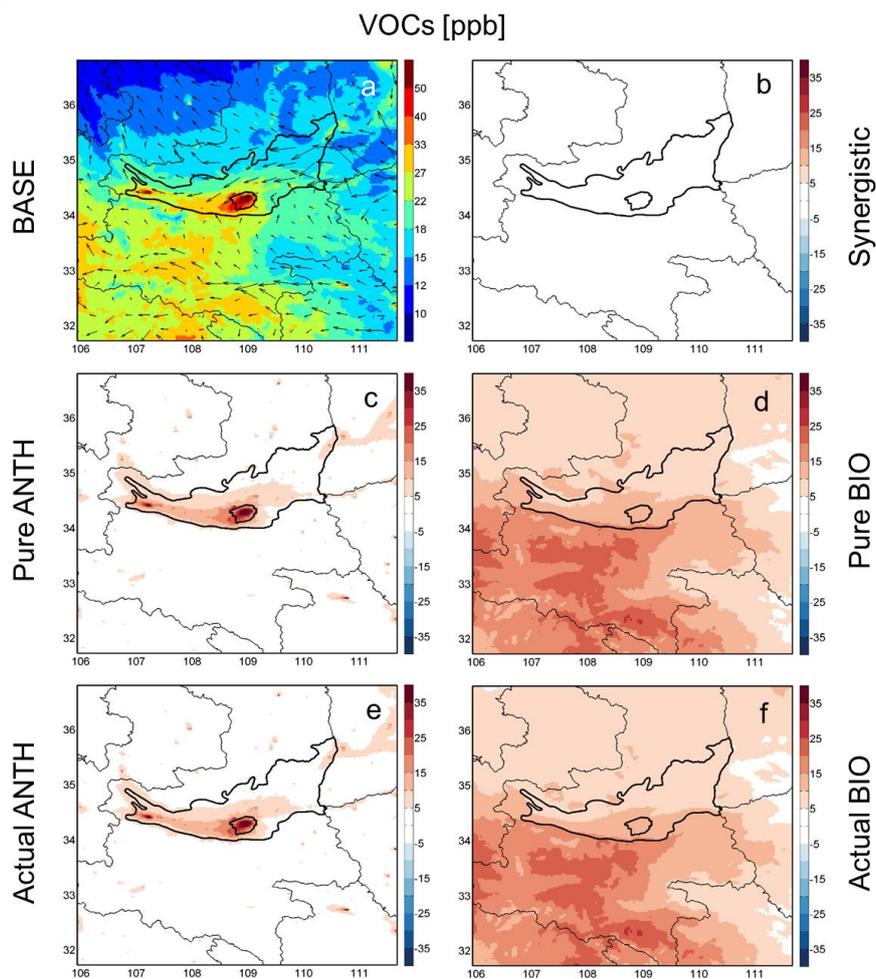


Figure 5. Spatial distributions of monthly mean concentrations of VOCs in August 2011. (a) is the result from the BASE simulation, overlaid with simulated wind vectors. (b)-(f) are simulated VOCs concentrations contributed from synergistic anthropogenic and biogenic, pure anthropogenic, pure biogenic, actual anthropogenic and actual biogenic sources, respectively.

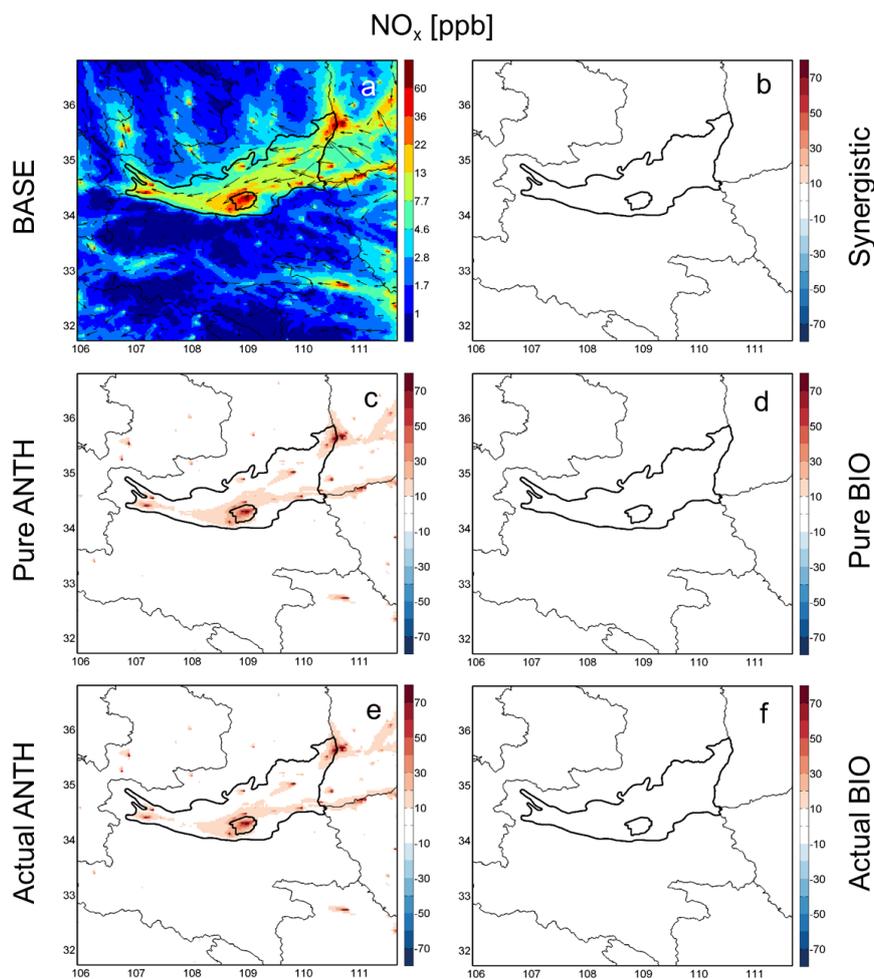


Figure 6. Spatial distributions of monthly mean concentrations of NO_x in August 2011. (a) is the result from the BASE simulation, overlaid with simulated wind vectors. (b)-(f) are simulated NO_x concentrations contributed from synergistic anthropogenic and biogenic, pure anthropogenic, pure biogenic, actual anthropogenic and actual biogenic sources, respectively.

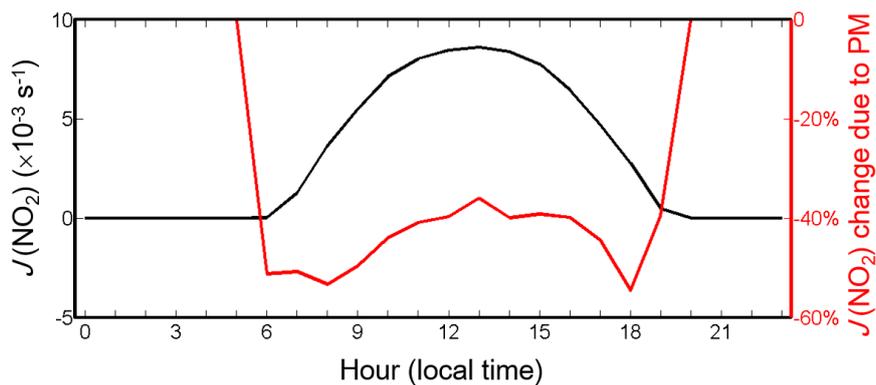


Figure 7. Diurnal variations of $J(\text{NO}_2)$ (black) and the changes in $J(\text{NO}_2)$ (red) averaged in urban Xi'an due to PM effects in August 2011.

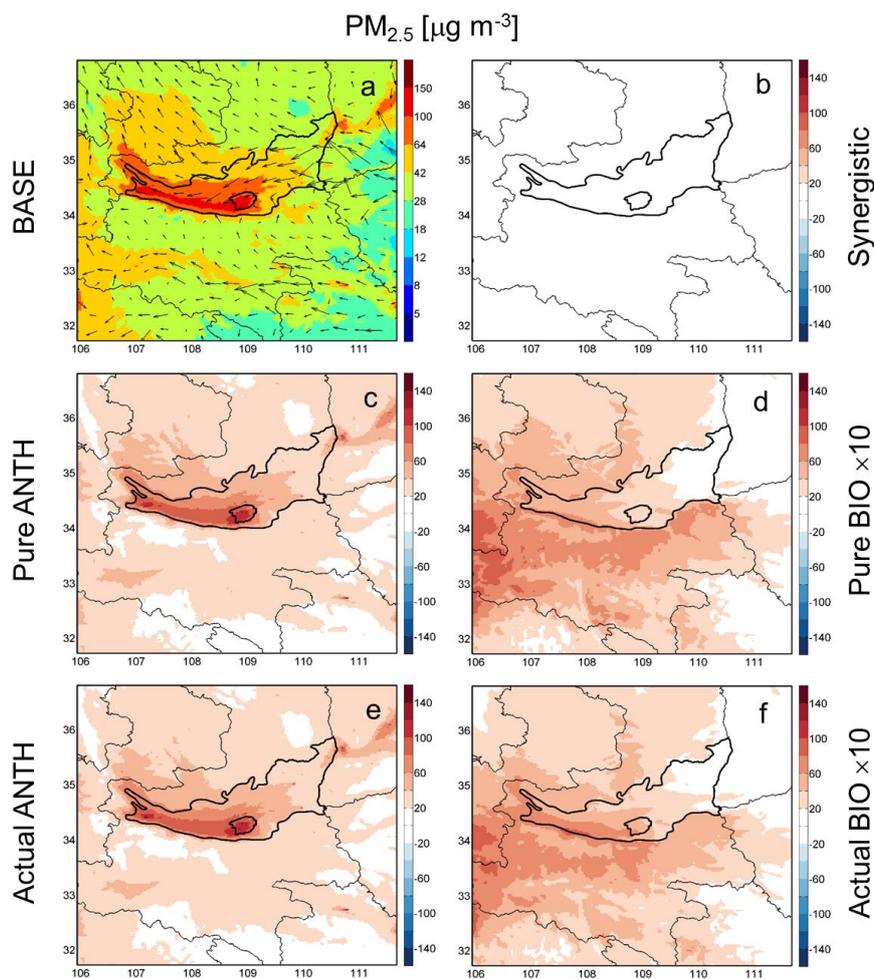


Figure 8. Spatial distributions of monthly mean concentrations of $PM_{2.5}$ in August 2011. (a) is the result from the BASE simulation, overlaid with simulated wind vectors. (b)-(f) are simulated $PM_{2.5}$ concentrations contributed from synergistic anthropogenic and biogenic, pure anthropogenic, pure biogenic, actual anthropogenic and actual biogenic sources, respectively.

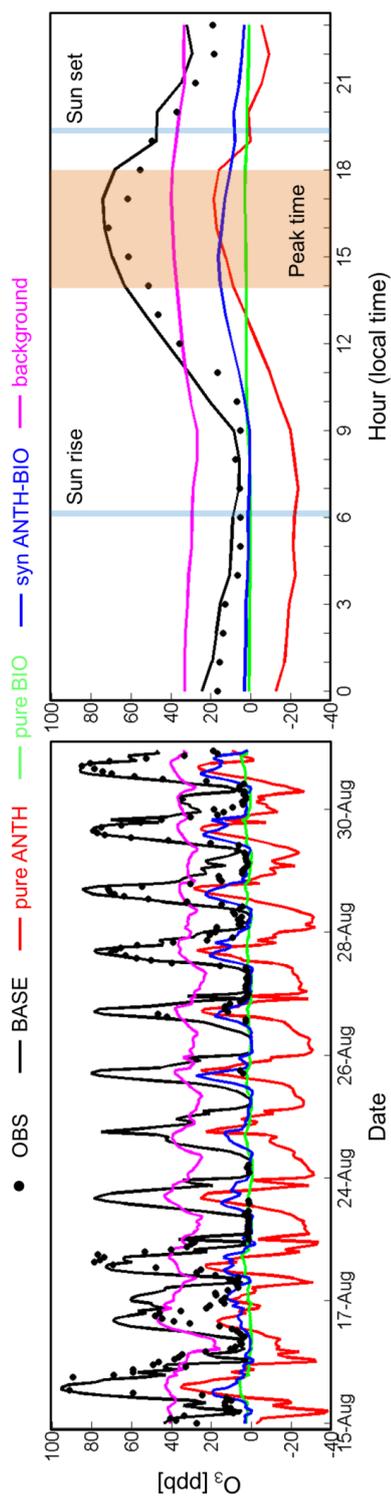


Figure 9. Temporal patterns of the simulated O₃ concentrations and the tested contributing components during the period from 15th to 30th August 2011, excluding the rainy days (18th -22nd August). The orange shadow (14:00-18:00) indicates daily O₃ peak time.

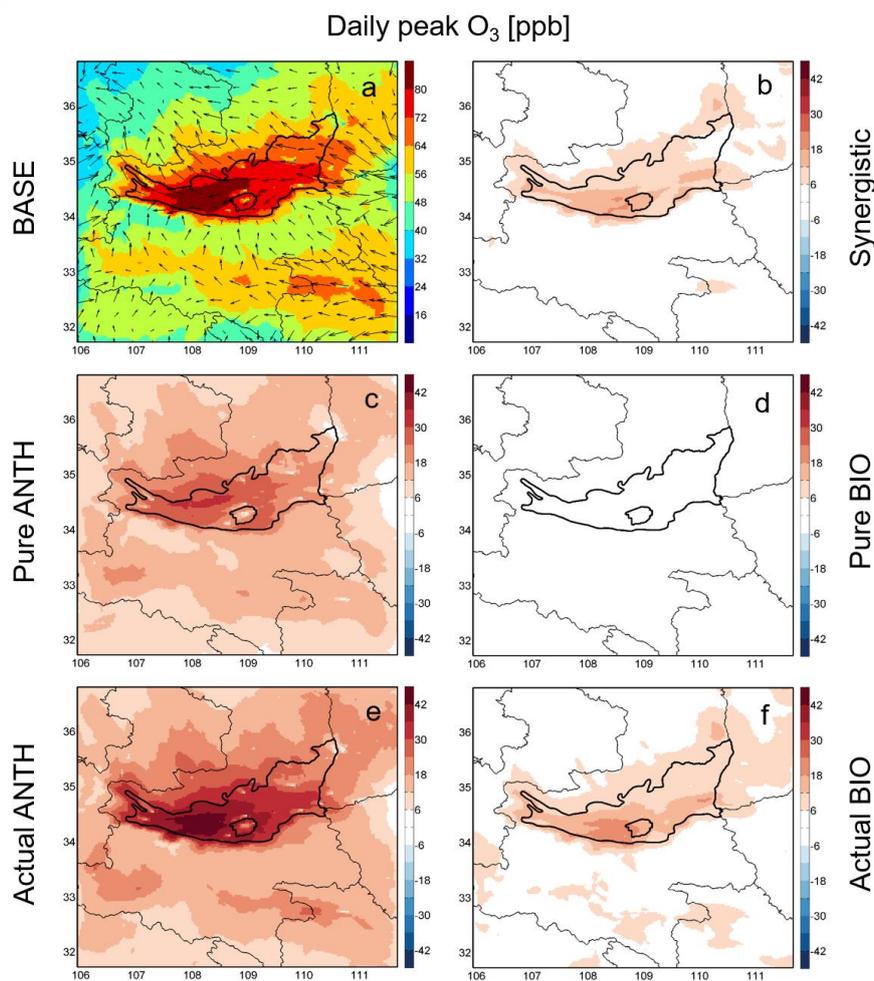


Figure 10. Spatial distributions of monthly mean concentrations of daily peak O₃ in August 2011. (a) is the result from the BASE simulation, overlaid with simulated wind vectors. (b)-(f) are simulated daily peak O₃ concentrations contributed from synergistic anthropogenic and biogenic, pure anthropogenic, pure biogenic, actual anthropogenic and actual biogenic sources, respectively.

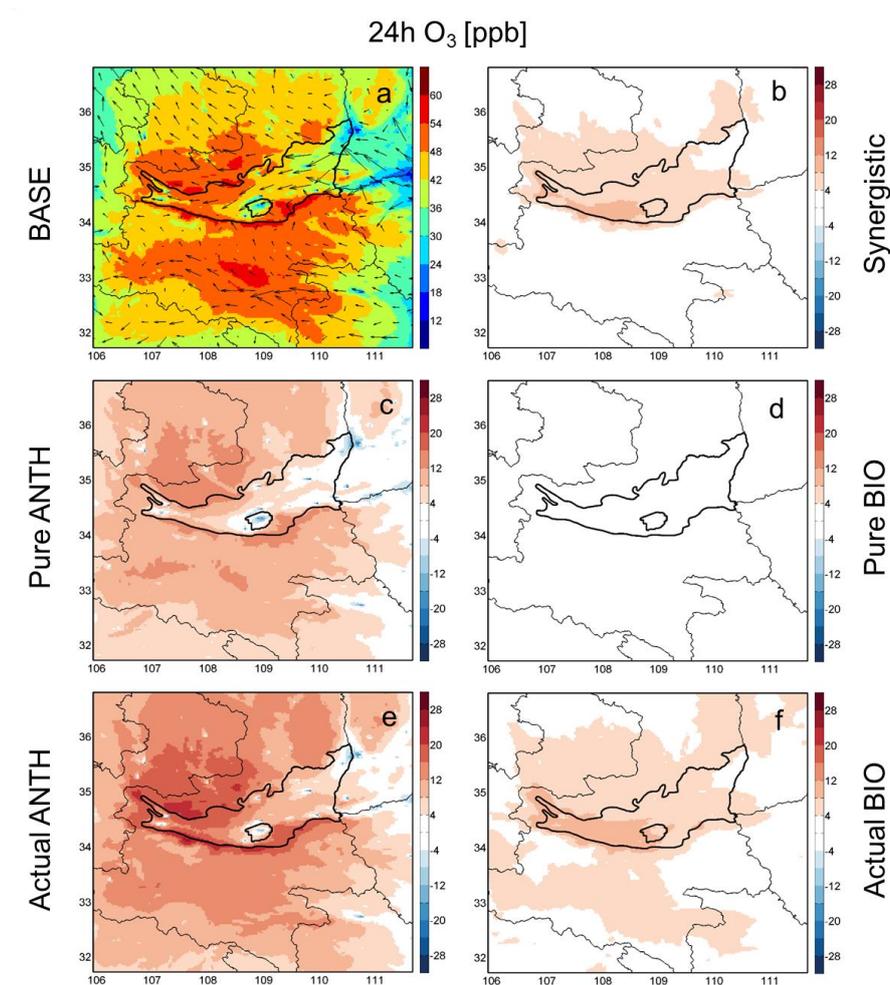


Figure 11. Spatial distributions of monthly mean concentrations of 24h averaged O₃ in August 2011. (a) is the result from the BASE simulation, overlaid with simulated wind vectors. (b)-(f) are simulated 24h averaged O₃ concentrations contributed from synergistic anthropogenic and biogenic, pure anthropogenic, pure biogenic, actual anthropogenic and actual biogenic sources, respectively.

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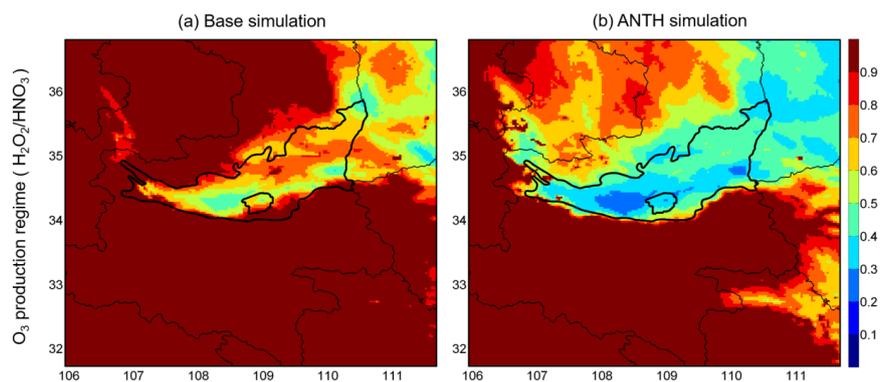


Figure 12. The monthly mean ratio of $\text{H}_2\text{O}_2/\text{HNO}_3$ during the daily O_3 peak time (14:00-18:00 local time) in August 2011 in the (a) Base simulation and (b) the simulation without biogenic sources.

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Table 1. Ambient biogenic VOCs observations in the Qinling Mountains during 6th – 7th August 2011

Site ^a	Date	Start Time ^b	Location	Isoprene (ppb)		Monoterpenes (ppb)		Dominant monoterpenes ^c
				Observation	Simulation	Observation	Simulation	
NBL	2011/8/6	10:20	33.78 E, 108.88 N	3.8	4.5	0.42	0.29	α -pinene
ZA	2011/8/6	12:44	33.40 E, 109.05 N	0.1	0.9	0.16	0.22	α -pinene, limonene, menthone
XY	2011/8/6	16:14	32.87 E, 109.40 N	1.0	0.3	0.24	0.13	α -pinene
AK	2011/8/7	09:45	32.71 E, 109.01 N	0.8	0.4	0.10	0.08	α -pinene
TJB	2011/8/7	13:00	32.99 E, 107.78 N	0.5	1.1	0.27	0.26	α -pinene
YS	2011/8/7	14:50	33.27 E, 107.73 N	1.6	0.9	0.04	0.32	α -pinene
Average				1.3	1.4	0.21	0.22	

^a Site names: NBL (Niubeiliang), ZA (Zhenan), XY (Xumyang), AK (Ankang), TJB (Tangjiaba), YS (Youshui)

^b The sampling duration is 30 minutes.

^c Other monoterpenes detected (0.1% to 9%) include tricyclene, α -thujene, camphene, sabinene, myrcene, α -phellandrene, Δ -carene, o-cymene, β -ocimene, cineole, isopulegol, isomenthone.

**Table 2.** Domain-wide amount of emissions in August 2011

	Anthropogenic (Gg mon ⁻¹)	Biogenic (Gg mon ⁻¹)	Total (Gg mon ⁻¹)
SO ₂	358	-	358
NO _x	110	2.1	112
NH ₃	69.0	-	69.0
PM _{2.5}	163	-	163
VOCs	72.2	204	276
Isoprene	<0.1	157	157
Monoterpenes	-	22.8	22.8
Alkanes	34.4	5.4	39.8
Alkenes	21.3	4.9	26.2
Aromatic	11.5	-	11.5
Carbonyls	4.5	12.1	16.6
Organic acids	0.5	1.5	2.0



Table 3. Summary of different simulation settings and definitions of the various contributions from anthropogenic and/or biogenic sources.

Simulation	Simulation results	Anthropogenic emission	Biogenic emission
BASE	$f_{\text{anth-bio}}$	✓	✓
ANTH	f_{anth}	✓	✗
BIO	f_{bio}	✗	✓
NEITHER	f_0	✗	✗
Contribution			
	$f_{\text{anth-bio}} - f_{\text{bio}}$	Actual contribution of anthropogenic emissions	
	$f_{\text{anth-bio}} - f_{\text{anth}}$	Actual contribution of biogenic emissions	
	$f_0 = f_0$	The contribution of background transport	
	$f'_{\text{anth}} = f_{\text{anth}} - f_0$	Pure contribution of anthropogenic emissions	
	$f'_{\text{bio}} = f_{\text{bio}} - f_0$	Pure contribution of biogenic emissions	
	$f'_{\text{anth-bio}} = f_{\text{anth-bio}} - (f_{\text{anth}} + f_{\text{bio}}) + f_0$	Synergistic contribution of anthropogenic and biogenic emissions	



Table 4. Statistics of meteorological and air quality variables over the GZ basin in August 2011^a

	Mean		r ^d	NMB ^d	RMSE ^d
	Observation	Simulation			
Meteorology^b					
Wind speed (m s ⁻¹)	2.6	2.5	-	-6%	1.8
Temperature (°C)	25.1	24.2	0.86	4%	2.5
Relative humidity	73.6%	74.2%	0.72	1%	12%
Air quality^c					
NO _x (ppb)	47.0	46.6	0.36	-1%	18.1
O ₃ (ppb)	31.5	38.7	0.72	21%	8.1
PM _{2.5} (µg m ⁻³)	107	94.6	-	-12%	49.3

^a Averaged for the period from 15th to 30th August 2011, excluding the rainy days.

^b Meteorological data were obtained from the hourly surface measurements at Jinghe station (108.58 °E, 34.26 °N)

^c Air quality data were measured at the roof (107 m above ground) of the main building (108.98 °E, 34.25°N) on the campus of Xi'an Jiaotong University

^d r: correlation coefficient; NMB: normalized mean bias; RMSE: root mean square errors.



Table 5. The various contribution components of the simulated O₃ (and the precursors) and PM_{2.5} in August 2011

	NO _x [ppb]	VOCs [ppb]	O ₃ [ppb]		PM _{2.5} [μg m ⁻³]
			daily peak ^a	24h	
<i>The GZ basin</i>					
Base	11.1	24.5	74.1	44.4	65.1
Pure ANTH	11.0	8.0	22.6	5.0	52.0
Pure BIO	0.1	9.9	2.0	1.1	3.3
Actual ANTH	10.6	7.7	33.0	10.8	53.5
Actual BIO	-0.3	9.6	12.5	7.0	4.9
Syn ANTH-BIO	-0.4	-0.3	10.5	5.8	1.5
<i>Urban Xi'an</i>					
Base	30.1	44.8	74.7	38.7	102
Pure ANTH	30.3	26.4	19.1	-2.2	88.7
Pure BIO	0.15	12.4	2.6	1.4	3.4
Actual ANTH	29.6	26.2	33.4	4.6	91.1
Actual BIO	-0.6	12.2	16.8	8.2	5.8
Syn ANTH-BIO	-0.7	-0.2	14.3	6.8	2.4

^a Daily O₃ peak time is from 14:00 to 18:00 local time