Causes of a continuous summertime $\text{O}_3$ pollution event in Ji’nan, a central city in the North China Plain

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Abstract: In summer 2017, measurements of ozone ($\text{O}_3$) and its precursors were carried out at an urban site in Ji’nan, a central city in the North China Plain (NCP). A continuous $\text{O}_3$ pollution event was captured during August 4-11, with the maximum hourly $\text{O}_3$ reaching 154.1 ppbv. The $\text{O}_3$ pollution was associated with the uniform pressure field over the NCP, and was also aggravated by the low pressure trough on August 9-10. Model simulation indicated that local photochemical formation and regional transport contributed 14.0±2.3 and 18.7±4.0 ppbv/hr to $\text{O}_3$ increase during 09:00-15:00 local time (LT), respectively. In the evening, vertical transport dominated the $\text{O}_3$ sources with the contribution of 54.5±9.6 ppbv/hr. For local $\text{O}_3$ formation, the calculated OH reactivity of volatile organic compounds (VOCs) and carbon monoxide (CO) was comparable between $\text{O}_3$ episodes and non-episodes ($p>0.05$), so was the OH reactivity of...
nitrogen oxides (NO\textsubscript{x}). However, the ratio of OH reactivity of VOCs and CO to that of NO\textsubscript{x} increased from 2.0±0.4 s\textsuperscript{-1}/s\textsuperscript{-1} during non-episodes to 3.7±0.7 s\textsuperscript{-1}/s\textsuperscript{-1} during O\textsubscript{3} episodes, which resulted in the change of O\textsubscript{3} formation mechanism from VOC-limited regime (non-episodes) to transition area (O\textsubscript{3} episodes) where O\textsubscript{3} production rates were among the highest. Correspondingly, the simulated local O\textsubscript{3} production rate during O\textsubscript{3} episodes (maximum: 21.3 ppbv/hr) was markedly higher than that during non-episodes (p<0.05) (maximum: 16.9 ppbv/hr). Given that gasoline and diesel exhaust made great contributions to O\textsubscript{3} precursors and O\textsubscript{3} production rate, constraint on vehicular emissions is the most effective strategy to control O\textsubscript{3} pollution in Ji’nan. Specifically, 10% reduction of diesel and gasoline exhaust led to a decrease of the simulated O\textsubscript{3} production rate of 0.58 and 0.47 ppbv/hr, respectively. Both the observation and model simulation imply that the NCP is a source region of tropospheric O\textsubscript{3}, and may “export” photochemical pollution to the surrounding areas.

**Keywords:** Ozone, local formation, regional transport, volatile organic compound, North China Plain

1 Introduction

Air pollution in the North China Plain (NCP), the largest alluvial plain of China consisting of Beijing, Tianjin and many cities in Hebei, Shandong, and Henan provinces, has attracted much attention of researchers in recent years. While the annual average concentration of PM\textsubscript{2.5} (particulate matters with aerodynamic diameter less than or equal to 2.5 μm) has been reduced under concerted efforts on emission restrictions (Zhang et al., 2015; Lang et al., 2017), the tropospheric ozone (O\textsubscript{3}) pollution, which is less visible than haze but may be equivalently harmful to human health, is still severe. At a regional receptor site of the NCP in a mountainous area north of Beijing, Wang et al. (2006) reported the maximum hourly O\textsubscript{3} of 286 ppbv. A year-round observation of O\textsubscript{3} at 10 urban sites in Beijing also revealed high O\textsubscript{3} concentrations through May to August (Wang et al., 2015a). Hourly O\textsubscript{3} mixing ratios of up to 120 ppbv were reported on Mt. Tai, the highest mountain in the NCP (1534 m a.s.l.) (Gao et al., 2005). This indicates the significant photochemical O\textsubscript{3} pollution over the entire NCP. Moreover, O\textsubscript{3} has been increasing in the NCP during the last decades (Zhang et al., 2014; Zhang et al., 2015). The increase rate of O\textsubscript{3} at an urban site in Beijing from 2005 to 2011 was quantified as 2.6 ppbv/year (Zhang et al., 2014), comparable to that (1.7-2.1 ppbv/year) at Mt. Tai in the summer between 2003 and 2015.
The severe O$_3$ pollution in the NCP may not only result from the intensive emissions of precursors but also relate to the synoptic systems and topographic features in this region (Chen et al., 2009; Zhang et al., 2016). For example, the strong photochemical production of O$_3$ in urban plumes of Beijing was found by Wang et al. (2006), while the contribution of regional transport was revealed by the enhanced O$_3$ production at a rural site in the NCP under southerly winds (Lin et al., 2008). Through the review of synoptic systems in the NCP from 1980 to 2013, Zhang et al. (2016) concluded that the air quality was generally unhealthy under weak East Asian Monsoons. Moreover, a decadal statistical analysis indicated that meteorological factors explained ~50% of the O$_3$ variations in Beijing (Zhang et al., 2015). Hence, comprehensive studies on the physical and chemical processes influencing O$_3$ pollution are urgent in the highly populated and industrialized NCP.

Volatile organic compounds (VOCs), carbon monoxide (CO) and nitrogen oxides (NO$_x$) are key precursors of tropospheric O$_3$ (Crutzen, 1973; Chameides and Walker, 1973; Carter, 1994; Carter et al., 1995). The general chemical reactions R(1) - R(5) show the production of O$_3$ from the OH initiated oxidation of hydrocarbons (RH) (Jenkin et al., 1997; Atkinson, 2000; Jenkin and Clemitshaw, 2000).

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\begin{align*}
\text{RH} + \text{OH} + \text{O}_2 & \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad (\text{R1}) \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \quad (\text{R2}) \\
\text{RO} + \text{O}_2 & \rightarrow \text{Carbonyls} + \text{HO}_2 \quad (\text{R3}) \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \quad (\text{R4}) \\
\text{NO}_2 + \text{O}_2 + hv & \rightarrow \text{O}_3 + \text{NO} \quad (\text{R5})
\end{align*}
\]

The production of O$_3$ is generally limited by VOCs or NO$_x$ or co-limited by both VOCs and NO$_x$, depending upon the air profiles, particularly the relative OH reactivity of VOCs and NO$_x$ (OH reactivity is the sum of the products of O$_3$ precursors concentrations and the reaction rate constants between O$_3$ precursors and OH). In general, VOCs and NO$_x$ are identified as the limiting reagents in O$_3$ formation in urban and remote areas, respectively, mainly due to the large quantities of NO$_x$ emissions from vehicles and power plants in cities (Sillman et al., 1990; Shao et al., 2009a). With the aid of a chemical transport model, Liu et al. (2010) indicated that O$_3$ formation was generally limited by NO$_x$ in most areas of central and western China, and switched from VOC-limited regime in January to NO$_x$-limited regime in July over eastern China.
Xue et al. (2014) found that O\textsubscript{3} formation was limited by VOCs in Shanghai (East China) and Guangzhou (South China) in spring, and limited by NO\textsubscript{x} in Lanzhou (West China) in summer. Alkenes, aromatics and carbonyls can be readily oxidized by oxidative radicals (e.g. OH) or photolyzed (applicable for carbonyls), leading to O\textsubscript{3} formation (Cheng et al., 2010; Guo et al., 2013). Therefore, the sources with a bulk emission of these VOCs generally make considerable contributions to the photochemical production of ground-level O\textsubscript{3}. For example, O\textsubscript{3} formation at an urban site in Hong Kong was most sensitive to xylenes emitted from solvent usage (Ling and Guo, 2014). Solvent based industry and paint solvent usage with high emissions of aromatics were responsible for more than half of O\textsubscript{3} formation potential in Shanghai (Cai et al., 2010). Carbonyls and alkenes accounted for 71-85% of the total OH reactivity of VOCs in Beijing (Shao et al., 2009b).

In addition to the chemical processes, O\textsubscript{3} pollution is also closely associated with meteorological conditions, which influence the formation, transport and accumulation of O\textsubscript{3}. Studies (Chan and Chan, 2000; Huang et al., 2005) indicated that tropical cyclone (typhoon) and continental anticyclone are the most common synoptic systems conducive of O\textsubscript{3} pollution in coastal cities of southern China. Many O\textsubscript{3} episodes in eastern China occurred under the control of the west Pacific subtropical high pressure (He et al., 2012; Shu et al., 2016). In the NCP, the summertime O\textsubscript{3} pollution is generally accompanied with a weak high pressure system (Wang et al., 2010). Furthermore, the terrain also plays a role in O\textsubscript{3} pollution. For example, the mountains in north and west of Beijing lead to upslope winds (valley breeze) in daytime, transporting polluted air masses laden with O\textsubscript{3} from NCP to Beijing (Lin et al., 2008). Overall, the causes of O\textsubscript{3} pollution are generally complicated and need to be analyzed case by case.

Ji’nan, the capital of Shandong province, also suffers from heavy photochemical pollution. As early as 2000s, studies (Shan et al., 2008; Yin et al., 2009) reported the maximum hourly O\textsubscript{3} of 143.8 ppbv and 147.8 ppbv in June 2004 and 2005, respectively. Even higher O\textsubscript{3} (198 ppbv) was observed at a rural site downwind of Ji’nan in June 2013 (Zong et al., 2018). Given that O\textsubscript{3} is continuously increasing in China, O\textsubscript{3} pollution in Ji’nan needs to be investigated in detail. On one hand, Ji’nan is an important city in Shandong Peninsula with a high population density. The O\textsubscript{3} pollution in Ji’nan is a concern of local residents. On the other hand, Ji’nan is a good example representing the medium-sized cities in the NCP with dense population, intensive industrial
emission and outdated production capacity. It has been repeatedly confirmed that air pollution in these types of cities in the NCP has seriously deteriorated air quality in Beijing (Lin et al., 2008; Wang et al., 2010). Thus, O$_3$ pollution in Ji’nan is also a regional issue. Contradictory to the critical roles of the cities like Ji’nan in the NCP and the necessity of O$_3$ studies, our knowledge on O$_3$ pollution in the NCP (except for Beijing and Tianjin) is rather limited. To better understand O$_3$ pollution in the NCP, this study investigated the causes of an O$_3$ episode lasting for eight days in Ji’nan in the summer of 2017. The analyses presented here focus on the synoptic systems dominating Shandong Peninsula during this event; the chemical profiles of O$_3$ and O$_3$ precursors; and the simulation of factors contributing to O$_3$ in Ji’nan with the aid of a chemical transport model and a photochemical box model. In addition, we propose feasible O$_3$ control measures based on the source-resolved OH reactivity of VOCs and NO$_x$.

2 Methodology

2.1 Site description

The air quality monitoring and sample collection were carried out on the rooftop of a 7-story building on the campus of Shandong University from July 15 to August 14, 2017. The campus is located in the urban area of Ji’nan, and the site is about 50 m from a main road (Shanda South Road) outside the campus. Figure 1 shows the locations of the sampling site (36.68°N, 117.07°E, 22 m a.g.l.) and some surrounding urban air quality monitoring stations (AQMSs) set up by China National Environmental Monitoring Center (CNEMC). Also shown are the observed O$_3$ and monitored rainfall averaged over August 4-11, 2017 when O$_3$ episodes occurred in Ji’nan. It is noteworthy that the days with maximum hourly O$_3$ exceeding 100 ppbv (Grade II of National Ambient Air Quality Standard) were defined as O$_3$ episode days. O$_3$ data in hourly resolution at the AQMSs were obtained from the website of CNEMC (http://www.cnemc.cn/).
Figure 1 Locations of the sampling site and the CNEMC AQMSs (colored circles in the left panel). Left panel color scale: Observed O$_3$ at 14:00 LT averaged over August 4-11, 2017. The location of the sampling site is overlapped with the nearest AQMS in Ji’nan. Right panel: Rainfall distribution, in millimeters (mm), averaged over August 4-11, 2017.

2.2 Air quality monitoring and sample collection

2.2.1 Continuous monitoring of air pollutants and meteorological parameters

O$_3$, NO and NO$_2$ were continuously monitored at the sampling site between July 15 and August 14, 2017. The air was drawn through a 4 m Teflon tube by the pumps in the trace gas analyzers with the total flow rate of 2 L/min (1.4 L/min for O$_3$ analyzer and 0.6 L/min for NO$_x$ analyzer). The inlet was located ~1 m above the rooftop of the 7-story building (~22 m a.g.l.). O$_3$ and NO/NO$_x$ were detected with a UV photometric based analyzer and a chemiluminescence NO-NO$_2$-NO$_x$ analyzer, respectively. NO$_2$ was calculated from the difference between NO and NO$_x$.

Studies indicated that NO$_2$ monitored with chemiluminescence was generally overestimated due to the conversion of other nitrogen containing compounds to NO by molybdenum oxide catalysts (McClenny et al., 2002; Dunlea et al., 2007; Xu et al., 2013). The positive interference is more significant in more aged air masses where peroxyacetyl nitrate (PAN), nitric acid (HNO$_3$) and alkyl/ multifunctional alkyl nitrates (ANs) are abundant (Dunlea et al., 2007). The average overestimation of NO$_2$ was 22% in Mexico City, which even increased to 50% in the afternoon (Dunlea et al., 2007). Though comparable or even higher overestimations were identified at the
suburban and mountainous sites in China, Xu et al. (2013) suggested that the chemiluminescence monitors overestimated NO$_2$ by less than 10% in urban areas with fresh emission of NO$_x$. As described in section 2.1, our sampling site was located in the urban area of Ji’nan and was only ~50 m to a main road. Therefore, we infer that NO$_2$ might not be significantly overestimated in this study. However, the influences of the overestimation on the findings were still discussed qualitatively where necessary.

The hourly concentrations of sulfur dioxide (SO$_2$) and CO were acquired from a nearest AQMS of CNEMC which is ~1 km from our sampling site. Year-round monitoring of inorganic trace gases was conducted at this AQMS, where the air was drawn into the analytical instruments at a flow rate of 3 L/min through an inlet, ~1 m above the rooftop of a 5-story building (~ 16 m a.g.l.). Table S1 provides the details of the trace gas analyzers used in this study, including the instrumental model, resolution, accuracy, precision and detection limit. The hourly concentrations of O$_3$ and NO$_2$ (NO data was not available on CNEMC website) measured at our sampling site agreed well with those reported at the AQMS, with the slope of 1.04 ($R^2 = 0.82$) and 1.13 ($R^2 = 0.71$) for O$_3$ and NO$_2$ in the linear least square regressions, respectively (Figure S1). Due to the instrumental differences and/or differences in sources and sinks of air pollutants at the two sites, the agreements were worse at low mixing ratios for both O$_3$ and NO$_2$. Therefore, we only used SO$_2$ and CO monitored at the nearest AQMS in this study, which had lower photochemical reactivity than O$_3$ and NO$_2$, and might be more homogeneous at a larger scale.

In addition, the meteorological parameters, including wind speed, wind direction, pressure, temperature and relative humidity were monitored by a widely used weather station (China Huayun group, Model CAWS600). The daily total solar radiation was obtained from the observations at a meteorological station in Ji’nan (36.6°N, 117.05°E, 170.3 m a.s.l), 9 km to our sampling site.

2.2.2 Sample collection and chemical analysis

During the real-time measurement of trace gases, offline VOC and oxygenated VOC (OVOC) samples were collected on 9 selective days (i.e., July 20 and 30, August 1, 4-7 and 10-11), referred to as VOC sampling days hereafter. The days were selected to cover the periods with relatively high and low levels of O$_3$. The high O$_3$ days were forecasted prior to sampling based on the numerical simulations of meteorological conditions and air quality. In total, 6 out of 9
VOC/OVOC sampling days were O$_3$ episode days with the maximum hourly O$_3$ ranging from 100.4 to 154.1 ppbv. On each day (regardless of episode or non-episode), 6 VOC/OVOC samples were collected between 08:00 and 18:00 local time (LT) every 2 hours with the duration of 1 hour for VOC and 2 hours for OVOC samples. VOC samples were collected with 2 L stainless steel canisters which were cleaned and evacuated before sampling. A flow restrictor was connected to the inlet of the canister to guarantee 1 hour sampling. OVOC were sampled with the 2,4-dinitrophenylhydrazine (DNPH) cartridge, in front of which an O$_3$ scrubber was interfaced to remove O$_3$ in the air. A pump behind the DNPH cartridge drew the air at a flow of 500 L/min. After sampling, all the DNPH cartridges were stored in a refrigerator at 4 °C until chemical analysis.

VOC samples were analyzed with a gas chromatograph-mass selective detector/flame ion detector/electron capture detector system (Colman et al., 2001). In total, 85 VOCs, including 59 hydrocarbons, 19 halocarbons and 7 alkyl nitrates, were quantified. The overall ranges of the detection limit (DL), accuracy and precision for VOCs analysis were 1-154 pptv, 1.2-19.8% and 0.1-17.9%, respectively. The analysis results given by this system have been compared with those analyzed by UCI and good agreements were achieved (Figure S2). OVOC samples were eluted with 5 mL acetonitrile, followed by analysis with the high performance liquid chromatography. The DL, accuracy and precision for all OVOCs analysis were within the range of 3-11 pptv, 0.32-0.98% and 0.01-1.03%, respectively.

2.3 Model configuration

2.3.1 Chemical transport model

To analyze the processes contributing to high O$_3$ in Ji’nan, a chemical transport model, the Weather Research Forecast-Community Multi-scale Air Quality (WRF-CMAQ), was utilized to simulate O$_3$ in this study. WRF v3.6.1 was run to provide the offline meteorological field for CMAQ v5.0.2. A two-nested domain was adopted with the resolution of 36 km (outer domain) and 12 km (inner domain), respectively. As shown in Figure S3, the outer domain covered the entire continental area of China aiming to provide sufficient boundary conditions for the inner domain, which specifically focused on eastern China.
We used the 2012-based Multi-resolution Emission Inventory for China (MEIC) to provide anthropogenic emissions of air pollutants, which was developed by Tsinghua University specific for China, with the grid resolution of 0.25°×0.25° (Zhang et al., 2007; He, 2012). Five emission sectors, namely transportation, agriculture, power plant, industry and residence were included in MEIC. The emission inventory was linearly interpolated to the domains with consideration of the earth curvature effect. For grids outside China, the air pollutant emissions were derived from INTEX-B (Intercontinental Chemical Transport Experiment-Phase B) Asian emission inventory (Zhang et al., 2009). Consistent with many previous studies (Jiang et al., 2010; Wang et al., 2015b), the Model of Emissions of Gases and Aerosols from Nature (MEGAN) was used to calculate the natural emissions. The physical and chemical parameterizations for WRF-CMAQ were generally identical to those described in Wang et al. (2015b), with some improvements. Firstly, the carbon bond v5 with updated toluene chemistry (CB05-TU) was chosen as the gas phase chemical mechanism (Whitten et al., 2010). Secondly, a single-layer urban canopy model (Kusaka and Kimura, 2004) was used to model the urban surface-atmosphere interactions. Thirdly, the default 1990s U.S. Geological Survey data in WRF was replaced by adopting the 2012-based moderate resolution imaging spectroradiometer (MODIS) land cover data for eastern China. The substitution was performed to update the simulation of boundary meteorological conditions (Wang et al., 2007).

An integrated process rate (IPR) module incorporated in CMAQ was used to analyze the processes influencing O₃ concentration. Through solving the mass continuity equation established between the overall change of O₃ concentration with time and the change of O₃ concentration caused by individual processes, including horizontal diffusion (HDIF), horizontal advection (HADV), vertical diffusion (VDIF), vertical advection (VADV), dry deposition (DDEP), net effect of chemistry (CHEM) and cloud processes (CLD), the contributions of the processes to O₃ variation rate were determined. Note that the estimate of CHEM is influenced by the estimate of O₃ precursor emissions, the simulation of meteorological conditions and the chemical mechanism, all the three aspects should be taken into account wherever CHEM is discussed. The IPR analysis has been widely applied in process diagnosis of O₃ pollution (Huang et al., 2005; Wang et al., 2015b).

2.3.2 Photochemical box model
A Photochemical Box Model incorporating the Master Chemical Mechanism (PBM-MCM) was used to study the in situ \( \text{O}_3 \) chemistry, in view of the detailed (species-based) descriptions of VOC degradations in the MCM (Saunders et al., 2003; Lam et al., 2013). The PBM model was localized to be applicable in Ji’nan, with the settings of geographic coordinates, sunlight duration and photolysis rates. The photolysis rates were calculated by the TUV model (Madronich and Floke, 1997). Specifically, the geographical coordinates, date and time were input into the TUV model, initializing the calculation of solar radiation with the default aerosol optical depth (AOD), cloud optical depth (COD), surface albedo and other parameters. Then, COD was adjusted to make the calculated daily total solar radiation progressively closer to the observed value. When the difference between the calculated and observed solar radiation were less than 1\%, the input parameters with the adjusted COD were accepted. Based on the settings, the hourly solar radiations and the photolysis rates of \( \text{O}_3 \) (\( J(\text{O}^1\text{D}) \)) and \( \text{NO}_2 \) (\( J(\text{NO}_2) \)) were calculated by the TUV model, and applied to PBM-MCM for \( \text{O}_3 \) chemistry modelling. Table S2 shows the daily maximum \( J(\text{O}^1\text{D}) \) and \( J(\text{NO}_2) \) on the VOC sampling days. The MCM v3.2 (http://mcm.leeds.ac.uk/MCM/) used in the present model consists of 17,242 reactions among 5,836 species. The measurements of \( \text{O}_3 \) and its precursors at 00:00 on each day were used as the initial conditions for each day’s modelling. The initial \( \text{O}_3 \), as the \( \text{O}_3 \) left over from the days before the modelling day, accounted for a part of the primary OH production. Hourly concentrations of 46 VOCs, 4 OVOCs and 4 trace gases (\( \text{SO}_2 \), \( \text{CO} \), \( \text{NO} \) and \( \text{NO}_2 \)), as well as hourly meteorological parameters (temperature and relative humidity) were input into the model, so that the model was constrained to observations. The hourly observed \( \text{O}_3 \) were not input, as it was the species to be modeled. The Freon, cycloalkanes and methyl cycloalkanes with low \( \text{O}_3 \) formation potentials were not included in model input. Also omitted were the species whose concentrations were lower than the detection limits in more than 20\% of the samples, such as the methyl hexane and methyl heptane isomers. For the hours when measurement data were not available, the concentrations were obtained with linear interpolation. Some secondary species, such as formaldehyde (HCHO), acetaldehyde and acetone, were input into the model to constrain the simulation. Since other secondary species, *e.g.*, PAN and HNO_3 were not observed in this study, their concentrations were calculated by the model. Dry deposition was considered for all the chemicals by setting the deposition velocities identical to those in Lam et al. (2013). Since
NO and NO\textsubscript{2} were separately measured and input into the model, which experienced different reactions as described by the species-based chemical mechanisms.

The simulations were separately carried out on all the VOC sampling days. To spin-up the model, the concentrations of air pollutants and meteorological conditions which were the same as those on the day of interest were input into the model for 72-h simulation before the modelling on that day. The model treated the air pollutants to be well-mixed in the boundary layer, without consideration of dilution and transport. O\textsubscript{3} in the free troposphere was not considered either, due to the lack of O\textsubscript{3} observations above the boundary layer over Ji’nan. This might hinder the accurate reproduction of the observed O\textsubscript{3}, particularly on the days when advection and diffusion were strong. Since the model mainly described the in situ photochemistry, it was validated through comparison with the CHEM process simulated by WRF-CMAQ. The simulated O\textsubscript{3} production rates were output every hour, which were integrated values over every 3600 s (model resolution: 1 s). More details about the model configuration can be found in Lam et al. (2003) and Lyu et al. (2017).

2.3.3 Positive Matrix Factorization (PMF) model

PMF was employed to identify the sources of O\textsubscript{3} precursors. Details about the operation principles of PMF can be found in Paatero and Tapper (1994). Briefly, the model treats the matrix of input concentrations as the product of two matrixes (i.e., factor contribution and factor profile). Here, hourly concentrations of 31 VOCs, CO, NO and NO\textsubscript{2} in 54 samples were input into the model. The VOCs, which were common tracers of specific sources (e.g., isoprene for biogenic emissions), and had relatively high concentrations (detectable in at least 80% samples), were selected for source apportionment (termed as VOCs* hereafter). On average, VOCs* accounted for 79.5±11.7% of the total quantified VOCs (mean ± 95% confidence interval of the hourly values in the statistical period, same for all the other “a ± b” expressions elsewhere unless otherwise specified). The uncertainties of the input concentrations of O\textsubscript{3} precursors were set as $\frac{5}{6} \times DL$ and $\sqrt{(10\% \times \text{concentration})^2 + (0.5 \times DL)^2}$ for the concentrations lower than and higher than DL, respectively.

The model was run for 20 times with a random seed and the best resolution automatically given by the model was accepted. A total of 6 sources of O\textsubscript{3} precursors were resolved by PMF in this
study. The number of sources was chosen based on the criteria that the tracers indicating different sources were not allocated in the same source, and all the sources were interpretable according to the tracers. The Bootstrap method integrated in PMF was used to estimate the uncertainties of the modelling results.

3. Results and discussion

3.1 Overall characteristics of $O_3$ pollution in Ji’nan

Figure 2 shows the time-dependent variations of trace gases, the calculated OH reactivity of VOCs, CO and NO$_x$, and meteorological conditions on the VOC sampling days in Ji’nan (Hourly values of trace gases in the whole sampling period are shown in Figure S4). The OH reactivity of $O_3$ precursors instead of their absolute concentrations was analyzed in this study, because OH reactivity, which considers both the abundances of precursors and reaction rate constants between different precursors and OH, more appropriately indicates the potentials of different precursors in contributing to $O_3$ production. It should be kept in mind that OH reactivity still does not reflect the actual contributions of $O_3$ precursors to $O_3$ production, unlike what the box model is capable of (McDuffie et al., 2016). As shown in Figure 2, the OH reactivity of VOCs are grouped into those of carbonyls, biogenic VOCs (BVOCs), aromatics, alkenes and alkanes (Table S3 lists the VOC species included in these groups). The reaction rate constants between $O_3$ precursors and OH in calculation of OH reactivity were adopted from the MCM v3.2 (http://mcm.leeds.ac.uk/MCM/). The average total OH reactivity on VOC sampling days ($19.4\pm2.1$ s$^{-1}$) was comparable to that reported in New York ($19\pm3$ s$^{-1}$, Ren et al., 2003), Houston ($9\pm2$ s$^{-1}$, Mao et al., 2010) and Beijing ($15-27$ s$^{-1}$, Williams et al., 2016). Consistent with the previous studies in urban areas (Ren et al., 2003; Yang et al., 2016 and references therein), NO$_x$ was the largest contributor ($28.9\pm1.9\%$) to the total OH reactivity. Noticeably, $20.5\pm4.1\%$ of the total OH reactivity was attributable to BVOCs, which was much higher than the contributions in urban areas (<10%) reviewed by Yang et al. (2016). The elevated isoprene level ($1.5\pm0.2$ ppbv) under high temperature (mean: $31^\circ$C) might explain the considerable contribution of BVOCs to the total OH reactivity in this study.

According to Figure 2, the first three days were non-episodes, while the rest were all $O_3$ episodes with the highest $O_3$ of $154.1$ ppbv at 13:00 LT on August 10. It was found that the total OH reactivity of VOCs and CO ($OH\text{ reactivity}_{VOCs+CO}$) was comparable between $O_3$ episodes...
(14.8±2.0 s⁻¹) and non-episodes (12.2±3.0 s⁻¹), so was the OH reactivity of NOₓ (4.7±0.8 s⁻¹ and 6.9±1.9 s⁻¹ during episodes and non-episodes, respectively). Throughout the text, the statistics were averages of hourly values over the period of interest when comparisons were made unless otherwise specified. Here, the OH reactivity of VOCs and CO was considered together as their reactions with OH generally lead to O₃ production, in contrast to the anti-correlation between NOₓ and O₃ in VOC-limited regime due to the depletion of OH by NO₂ (OH + NO₂ → HNO₃).

Since NO₂ might be more overestimated on episode days due to the higher concentrations and greater interferences of HNO₃, PAN and ANs, the actual OH reactivity of NOₓ during episodes might be lower than during non-episodes. In fact, the high OH reactivity during non-episodes was mainly caused by high concentrations of O₃ precursors on July 30 and August 1.

As shown in Figure 2, the highest pressures (color of the wind vectors) throughout the sampling campaign were observed on these two days, which might suppress the dispersion of O₃ precursors. More importantly, the solar radiation was relatively weak and the temperature was low, particularly on July 30 when the maximum solar radiation and highest temperature was only 244 W/m² and 26.2 °C, respectively. This meant that photochemical consumption of O₃ precursors might be weakened on these days, causing the high OH reactivity of O₃ precursors.

Despite comparable OH reactivity between episodes and non-episodes, we found that the ratio of \( \frac{OH \text{ reactivity}_{VOCs+CO}}{OH \text{ reactivity}_{NOx}} \) during O₃ episodes (3.7±0.7 s⁻¹/s⁻¹) was higher (\( p<0.05 \)) than during non-episodes (2.0±0.4 s⁻¹/s⁻¹). Taking into account the greater overestimation of NO₂ on episode days, the difference of \( \frac{OH \text{ reactivity}_{VOCs+CO}}{OH \text{ reactivity}_{NOx}} \) between episodes and non-episodes might be even larger.

This indicated that O₃ formation was more limited by VOCs during non-episodes than during episodes. In fact, O₃ formation in Ji’nan switched to the transition area during episodes from the VOC-limited regime during non-episodes (see section 3.4.2). This might partially explain the building-up of O₃ on episode days, as O₃ production was generally the highest in the transition area. The contribution of BVOCs to total OH reactivity during O₃ episodes (24.0±5.7%) was much higher than during non-episodes (13.9±3.6%), which was likely due to more intensive isoprene emissions under stronger solar radiation and higher temperature during episodes (isoprene: 2.2±0.6 ppbv during episodes and 0.9±0.3 ppbv during non-episodes). Many studies have found that BVOCs are efficient O₃ producers due to their abilities to propagate radicals (Curci et al., 2009; Cheng et al., 2010). Keep in mind that the abundances of O₃ precursors were
also influenced by the meteorological conditions, in addition to emissions. We do not claim that
the change of \( \frac{[OH \text{reactivity}_{\text{VOC}+\text{CO}}]}{[OH \text{reactivity}_{\text{NO}x}}} \) was merely attributable to variations in emissions.

SO\(_2\) and CO were higher during non-episodes than during episodes \((p<0.05)\), due to the
accumulation of primary air pollutants on July 30 and August 1. While NO and NO\(_2\) were
respectively comparable between non-episodes and O\(_3\) episodes \((p>0.05)\), the ratio of NO\(_2\)/NO
increased substantially from 1.7±0.3 ppbv/ppbv during non-episodes to 3.0±0.4 ppbv/ppbv
during episodes \((p<0.05)\). This was likely attributable to more conversion of NO to NO\(_2\) under
higher levels of O\(_3\) and peroxy radicals during episodes, when the stronger solar radiation played
an important role in enhancing the formation of O\(_3\) and peroxy radicals. Nevertheless, the higher
average ratio of NO\(_2\)/NO on episode days was partially caused by the greater overestimation of
NO\(_2\) during episodes.

From the perspective of meteorological conditions, O\(_3\) episodes had relatively stronger solar
radiation, higher temperature, lower relative humidity and weaker winds \((p<0.05)\). This is
reasonable as O\(_3\) formation and accumulation are generally enhanced under these weather
conditions. As aforementioned, the solar radiation on July 30 was much weaker than those
during O\(_3\) episodes, which was probably the most critical factor leading to low O\(_3\) on this day.

Figure S5 shows the COD retrieved from the terra/MODIS (https://ladsweb.modaps.
eosdis.nasa.gov/search/imageViewer/1/MOD06_L2--61/2017-08-06/DB/Site:142/2873994172--
3) at 10:00 – 12:00 (local time) of the VOC sampling days. The terra/MODIS image revealed
thick cloud cover with high COD over Ji’nan on July 30, explaining the weak solar radiation. In
fact, obvious anti-correlation existed between solar radiation and the COD. The influences of
cloud cover/ COD and solar radiation on O\(_3\) pollution during the study period in Ji’nan are
discussed in section 3.2. Unlike many previous findings that O\(_3\) pollution was aggravated by high
pressure (Chan and Chan, 2000; Zhao et al., 2009), the sea-level pressure during O\(_3\) episodes
\((993.4±0.2\ \text{hPa})\) was significantly lower than during non-episodes \((996.1±0.4\ \text{hPa})\) in this study
\((p<0.05)\). When O\(_3\) reached its hourly maximum on August 10 \((154.1\ \text{ppbv})\), the pressure was at
its lowest value of the campaign \((990.2\ \text{hPa})\). The continuously severe O\(_3\) pollution event under
low pressure is further investigated below.
Figure 2 Time-dependent variations of trace gases, OH reactivity of \( \text{O}_3 \) precursors and meteorological parameters. Wind speed and wind direction were not monitored from 17:00 LT on August 5 to 23:00 LT on August 7 due to malfunction of the weather station. RX in the bottom panel is the OH reactivity of species/group X.

3.2 Synoptic processes and relationship with \( \text{O}_3 \) pollution

Figure 3 displays the average weather charts at 14:00 LT during \( \text{O}_3 \) episodes and non-episodes (weather charts on individual VOC sampling days are shown in Figure S6). Clearly, the temperature over Shandong Peninsula was much higher during \( \text{O}_3 \) episodes than non-episodes, which favored \( \text{O}_3 \) formation on episode days. Additionally, southerly and southwesterly winds originating from the inland areas (Hubei, Henan, and Anhui provinces) prevailed in central and western Shandong province during \( \text{O}_3 \) episodes. In contrast, the winds were generally from the sea or coastal region in Jiangsu province during non-episodes. \( \text{O}_3 \) and \( \text{O}_3 \) precursors might be transported to Ji’nan in the former cases. For the latter cases, though the winds were from relatively the clean sea and coastal region, the concentrations of \( \text{O}_3 \) precursors on July 30 and August 1 (non-episode days) were still high, which were mainly caused by weather conditions...
(high pressure, low temperature and low solar radiation), as discussed in section 3.1. Nevertheless, we believe that the incoming sea and coastal air at least did not aggravate air pollution in Ji’nan during non-episodes, including on July 30 and August 1. Further, we also noted that the winds changed direction from southwest to northwest around Ji’nan during O3 episodes. This meant that there might be a local circulation hampering the dispersion of air pollutants during episodes. Overall, the wind fields were more favorable for regional transport and accumulation of air pollutants in Ji’nan during episodes. It seems that the turning-round of the winds around Ji’nan was associated with the sea breeze from Bohai Bay, which might be one of the typical factors influencing air pollution in the Shandong Peninsula, like the convergence of continental air and sea breeze (from South China Sea) in Hong Kong (Fung et al., 2005; Lo et al., 2006). Unlike the weak mesoscale sea breezes originating from Bohai Bay during episodes, the synoptic winds from the open sea swept over the Shandong Peninsula and did not converge with the continental air during non-episodes, thus not a factor aggravating air pollution in Ji’nan.

In addition, Ji’nan was on the peripheral of a high pressure system over the Yellow Sea during non-episodes, which might drive the clean and humid oceanic air to Ji’nan. In contrast, Shandong Peninsula was under a uniform pressure field with the sea-level pressure of 1000-1001 hPa during O3 episodes, implying the relatively stagnant weather conditions unfavorable for the dispersion of air pollutants.

Figure 3 Weather chart at 14:00 LT averaged over (a) O3 episodes and (b) non-episodes. The red star represents Ji’nan. The dark black line is the boundary of Shandong province. Bohai Bay is located to the northeast of Shandong province. Numbers in the figure are sea-level pressures in unit of hPa.
To better understand the relationship between \( \text{O}_3 \) pollution and the synoptic systems, Table 1 summarizes the characteristics of synoptic system, weather condition and air mass origin on individual VOC sampling days. The weather charts for the surface level and 500 hPa on August 1, 4, 7, 10 and 13 are presented in Figures S6-S7, which showed the evolution of synoptic systems at different stages of the \( \text{O}_3 \) episodes. To identify the origins of air masses, the 48 hour backward trajectories of air masses are shown in Figure 4. The trajectories were computed using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model v 4.9. Each trajectory was calculated for 48 hours and the calculation was done every 6 hours (4 trajectories each day). Our sampling site (36.68° N, 117.07° E) was set as the starting point of the backward trajectories with the height of 500 m a.s.l. The discrepancy between the wind direction and origin of air masses, e.g. on August 1 and 11, was likely due to the air recirculation at the ground level.

It was found that Ji’nan was under the control of a Western Pacific Subtropical High pressure system (WPSH) on July 20 (weather chart on 500 hPa is not shown here), and the air masses arriving in Ji’nan originated from South China 48 hours prior (Figure 4). As anticipated, the WPSH caused high temperatures and the intensive solar radiation during the study period (maximum: 943 W/m\(^2\)) in Ji’nan (Figure 2), which was conducive to \( \text{O}_3 \) formation. However, the winds on July 20 were the strongest in the entire VOC sampling period, with the highest hourly wind speed of 3.9 m/s. The strong winds might facilitate the transport and dispersion of \( \text{O}_3 \) precursors and locally formed \( \text{O}_3 \) on July 20 (refer to the low levels of \( \text{O}_3 \), \( \text{O}_3 \) precursors and OH reactivity in Figure 2).

On July 30 and August 1, the WPSH moved southward and Ji’nan was under a uniform pressure field. The uniform pressure field was formed because Ji’nan was on the periphery of two low pressure systems (two rain belts as shown in Figure 1), i.e. one over Central China and another over North China (Figure S7). Thus, the pressure in Ji’nan was relatively high (997.1±0.3 hPa), compared to the south and north regions, which was defined as weak high pressure. This synoptic system lasted for several days until August 7, covering 2 non-episode days and 4 \( \text{O}_3 \) episode days. On July 30, Ji’nan featured very weak solar radiation (maximum: 244 W/m\(^2\)) and thick cloud cover (Figure 2 and Figure S5). The weak solar radiation might be primarily responsible for the low \( \text{O}_3 \) in Ji’nan on July 30. Though there was still some cloud cover over Ji’nan on August 1, the COD decreased relative to that on July 30 (Figure S5). Correspondingly,
the solar radiation increased to the level comparable to that on the O3 episode days. As a result, the hourly maximum O3 increased to 90.6 ppbv on August 1, though it was still an O3 attainment day. In addition, the temperature was relatively low on July 30 and August 1. Though the OH reactivity of O3 precursors on these days was comparable to or even higher than that on August 4-7 (Figure 2), the weak solar radiation and/or low temperature might not be conducive to O3 formation which explained the low O3 on these days. In contrast, continuously strong solar radiation with low COD (Figure 2 and Figure S5), high temperature and continental air masses (Figure 4) were observed on August 4-7, partially accounting for the consecutive O3 pollution days. In addition, despite the moderate levels of OH reactivity of O3 precursors on August 4-7, the higher ratio of $\frac{OH\text{ reactivity}_{VOC+CO}}{OH\text{ reactivity}_{NOx}}$ enabled stronger O3 production on these days (see sections 3.1 and 3.4.2).

On August 10, the rain belt over North China moved southward, forming a deep low pressure trough over the NCP (Figure S8 (d)). Ji’nan was behind the trough, indicating that there was strong downward air flow in Ji’nan on August 10. It is well known that low pressure trough is a typical synoptic system aggravating O3 pollution, due to the downward air flow behind the trough, which may bring O3 in the stratosphere and/or the upper troposphere to the ground (Chan and Chan, 2000). Moreover, there was nearly no cloud cover over the entire NCP on this day (Figure S5), causing strong solar radiation (maximum: 879 W/m$^2$, only second to those on July 20). Consequently, the highest O3 (154.1 ppbv) in this sampling campaign was observed on August 10. In addition, the in situ O3 production rate on this day was higher than on the non-episode days, even under the same meteorological conditions as those during non-episodes, due to the switch of O3 formation mechanism from VOC-limited regime to transition regime (see section 3.4.2). On August 11, the low pressure system continued to extend to the Yellow Sea. O3 decreased substantially on this day with the disappearance of the low pressure trough and the weakening of solar radiation, though the hourly maximum O3 still reached 100.4 ppbv. On the following days, it was rainy in Ji’nan and O3 decreased to low levels (Figure S4).

Table 1 Summary of the synoptic systems, weather conditions and air mass origins on VOC sampling days.

| Date | O3 maximum | Episode/non-episode | Synoptic system | Weather condition | Air mass origin |
|------|------------|---------------------|-----------------|------------------|----------------|
|      |            |                     |                 |                  |                |

On August 10, the rain belt over North China moved southward, forming a deep low pressure trough over the NCP (Figure S8 (d)). Ji’nan was behind the trough, indicating that there was strong downward air flow in Ji’nan on August 10. It is well known that low pressure trough is a typical synoptic system aggravating O3 pollution, due to the downward air flow behind the trough, which may bring O3 in the stratosphere and/or the upper troposphere to the ground (Chan and Chan, 2000). Moreover, there was nearly no cloud cover over the entire NCP on this day (Figure S5), causing strong solar radiation (maximum: 879 W/m$^2$, only second to those on July 20). Consequently, the highest O3 (154.1 ppbv) in this sampling campaign was observed on August 10. In addition, the in situ O3 production rate on this day was higher than on the non-episode days, even under the same meteorological conditions as those during non-episodes, due to the switch of O3 formation mechanism from VOC-limited regime to transition regime (see section 3.4.2). On August 11, the low pressure system continued to extend to the Yellow Sea. O3 decreased substantially on this day with the disappearance of the low pressure trough and the weakening of solar radiation, though the hourly maximum O3 still reached 100.4 ppbv. On the following days, it was rainy in Ji’nan and O3 decreased to low levels (Figure S4).
| Date       | Value | Type     | Weather Conditions                                                                 | Air Masses From                      |
|------------|-------|----------|------------------------------------------------------------------------------------|--------------------------------------|
| July 20, 2017 | 71.0  | Non-episode | Subtropical high, strong southwesterly winds                                       | Continental air masses from South China |
| July 30, 2017  | 57.6  | Non-episode | Uniform pressure field (weak high pressure), rain, fog, calm winds                  | Marine air masses                    |
| August 1, 2017 | 90.6  | Non-episode | Uniform pressure field (weak high pressure), northeasterly winds                    | Marine air masses                    |
| August 4, 2017  | 107.5 | Episode    | Uniform pressure field (weak high pressure), northeasterly winds                    | Continental air masses from Shandong province |
| August 5, 2017  | 128.2 | Episode    | Uniform pressure field (weak high pressure), calm winds                            | Continental air masses from Shandong province |
| August 6, 2017  | 116.9 | Episode    | Uniform pressure field (weak high pressure), southwesterly winds                   | Continental air masses mostly from Shandong province |
| August 7, 2017  | 126.9 | Episode    | Uniform pressure field (weak high pressure), calm winds                            | Continental air masses from the north |
| August 10, 2017 | 154.1 | Episode    | Low-pressure trough, calm winds                                                   | Continental air masses from the west |
| August 11, 2017 | 100.4 | Episode    | Subtropical high, southeasterly winds                                             | Continental air masses from the southwest |
Figure 4 Forty eight hour backward trajectories calculated every 6 hours, with Ji’nan (36.68°N, 117.07°E, 500 m a.g.l.) as the starting point. The trajectories are simulated by HYSPLIT v4.9. The water areas are highlighted in blue.

3.3 O₃ simulation and process analysis

To further clarify the causes of the continuous O₃ episodes in Ji’nan, WRF-CMAQ was utilized to simulate O₃ and the processes influencing O₃ concentrations. Figure 5 shows the hourly average simulated and observed O₃ on the VOC sampling days in Ji’nan. Overall, the model well reproduced the magnitudes and diurnal patterns of the observed O₃, except for the higher simulated O₃ on July 20 and the under-prediction of O₃ on August 1, 7 and 10. Due to inevitable uncertainties inherent in the chemical transport models, such as the uncertainties in emission inventory, meteorological simulation and chemical mechanisms (Hu et al., 2016), it is difficult to deduce the reasons for the discrepancies. However, the observation data revealed extremely high levels of some VOCs on the three days when O₃ was under-predicted. Specifically, 13.5 ppbv of ethene was observed at 14:00 LT on August 1. On August 7, 5.6 ppbv of isoprene, 16.2 ppbv of HCHO and 2.3 ppbv of hexanal were measured during 12:00 – 14:00 LT. On August 10, 22.7 ppbv of propene and 12.7 ppbv of i-butane were recorded at 08:00 and 16:00 LT, respectively. It
is noteworthy that these mixing ratios were 5 – 10 times higher than their averages. Further, most of these VOCs are highly reactive in O₃ photochemistry and may make great contributions to local O₃ production. With the setting of constant emissions of O₃ precursors, WRF-CMAQ did not reproduce these extremely high levels of VOCs, which was a plausible reason for the under-prediction of O₃ on August 1, 7 and 10. Ji’nan was behind a low pressure trough on August 9 – 10. However, vertical transport was simulated to make negative contributions to O₃ between 10:00 LT and 18:00 LT, according to the process analysis. In addition, the simulated O₃ in the upper atmosphere on August 10 was relatively low compared to that on August 5, 6 and 9 (Figure S9). Namely, the model might fail to reproduce the O₃ enhancement driven by the low pressure trough on August 10.

The process analysis indicated that horizontal and vertical transport dominated the sources of O₃ at noon (10:00-12:00 LT) and the other times of July 20, respectively. While vertical transport might explain the high O₃ at night (Figure 2), it was not likely that horizontal transport built up O₃ at noon, because the southwesterly airflow originated from South China and passed central China (Figure 4) where O₃ values were relatively low on that day (high O₃ occurred in Hebei province in the northwest). Therefore, the overestimate of the transport effect led to the higher simulated O₃ on July 20.

Despite these discrepancies, overall the observed O₃ at the sampling site was well reproduced. In addition, the spatial distribution of the simulated O₃ was highly consistent with the observed O₃ distribution, as shown in Figure 6. The average concentrations of the simulated VOCs were also compared with the observations (Figure S10). While the day-to-day and diurnal variations of the observed VOCs were not well reproduced (not shown), which is a proverbial drawback of the WRF-CMAQ, the model reasonably simulated the magnitudes of VOCs. Moreover, the averages of the observations (Avg. Obs.) and simulations (Avg. Sim.), difference between Avg. Obs. and Avg. Sim. (Diff.), root mean square error (RMSE), normalized mean bias (NMB), normalized mean error (NME) and index of agreement (IOA) were calculated to reflect the agreements between the simulated and observed temperature (Temp.), relative humidity (R.H.), wind speed (W.S.), pressure (Press.), NO₂ and O₃, as listed in Table 2. Generally, the lower Diff., RMSE, NMB and NME, but higher IOA indicate better agreement between the simulated and observed values (Willmott et al., 1985). The validation of the simulations of air pollutants was carried out...
at 8 AQMSs of CNEMC in and around Ji’nan, and at the sampling site, while the meteorological parameters monitored at 6 airports in eastern and northern China and at the sampling site were used to validate the simulated meteorological conditions. The statistics calculated in this study were well within the ranges of those reported in previous studies involving WRF-CMAQ simulations (Table 2) (Jiang et al., 2010; Wang et al., 2015b), suggesting good performance of the model in reproducing the meteorological conditions and air pollutants. Thus, the simulated results were accepted for further analyses.

Figure 5 Hourly average mixing ratios of the WRF-CMAQ simulated and observed O₃ in Ji’nan. The grey area shows the minimum and maximum simulated O₃ at the sampling site and 8 adjoining grids (12×12 km² for each grid).
Figure 6 Comparison between the spatial distributions of (a) the WRF-CMAQ simulated O$_3$ and (b) the observed O$_3$ at 14:00 LT averaged over August 4-11. The observed O$_3$ was acquired from the AQMSs of CNEMC.

Table 2 Statistical comparison of the WRF-CMAQ simulated and observed meteorological parameters, O$_3$ and NO$_2$. The comparisons were made for the hourly data in 24 hours on all the VOC sampling days.

| Meteorological parameter/ Air pollutant | Avg. Obs. | Avg. Sim. | Diff. | RMSE | NMB | NME | IOA |
|----------------------------------------|-----------|-----------|-------|------|-----|-----|-----|
| Temp. (°C)                             | 30.0      | 30.7      | 0.7   | 2.4  | 0.02| 0.06| 0.89|
| R.H. (%)                               | 72.7      | 67.5      | -5.2  | 14.4 | -0.06| 0.15| 0.82|
| W.S. (m/s)                             | 2.8       | 3.3       | 0.5   | 1.5  | 0.38| 0.56| 0.74|
| Press. (hPa)                           | 1000.5    | 998.8     | -1.7  | 4.0  | -0.002| 0.003| 0.56|
| NO$_2$ (ppbv)                          | 26.7      | 28.4      | 1.7   | 16.7 | 0.18| 0.58| 0.73|
| O$_3$ (ppbv)                           | 62.8      | 52.4      | -10.4 | 24.0 | -0.07| 0.48| 0.89|

The IPR analysis quantifies the contributions of different processes to the O$_3$ production rate, as shown in Figure 7. HDIF and HADV were summed as horizontal transport (HTRA), and the vertical transport (VTRA) was a total representative of VDIF and VADV. It was found that chemical reactions generally led to O$_3$ decrease during non-episodes. The negative contributions of chemical reactions on July 20 coincided with the very low concentrations of O$_3$ precursors and the flat diurnal cycle of O$_3$ (Figure 2). The chemical destruction of O$_3$ on July 30 and August 1 might be related to the relatively weak solar radiation and low temperature, which inhibited the in situ photochemical reactions. In fact, the negative chemical effect should be considered as the titration of NO to regionally-transported and/or background O$_3$ and the conversion of O$_3$ to NO$_2$ near NO sources in urban areas (Beck and Grennfelt, 1994; Sillman, 1999). Conversely, the combined effect of horizontal and vertical transport was to increase O$_3$.

During O$_3$ episodes, chemical reactions made positive contributions to O$_3$ production between 09:00 LT and 15:00 LT, with the average hourly O$_3$ production rate of 14.0±2.3 ppbv/hr from August 4 to August 11. At the same time, O$_3$ was also elevated by transport at an average rate of...
18.7±4.0 ppbv/hr, when the negative effect of vertical transport (-40.8±20.2 ppbv/hr) was reversed by horizontal transport (59.5±19.8 ppbv/hr). The negative contribution of vertical transport to \(O_3\) in these hours might be caused by the updraft with the increase of temperature in the city. The \(O_3\) enhancement by horizontal transport could be explained by the westerly to northerly airflows (Figure 4) and the high \(O_3\) in the areas where the airflows originated or passed (Figure 6). Note that \(O_3\) transported to Ji’nan was still from the NCP, hence we concluded that the NCP was an \(O_3\) source in this case. In fact, the transport of air pollutants (including \(O_3\)) from the lower troposphere over the NCP to the free troposphere and further to northeast China was previously identified by Ding et al. (2009), who suggested that the pollutants could be even transported to North America and the Arctic.

During 16:00-08:00 LT on \(O_3\) episode days, \(O_3\) was titrated and chemically consumed at the rate of 49.4±6.3 ppbv/hr. This was reasonable in view of the fresh vehicular emissions (particularly \(NO_x\)) in the morning and evening rush hours, when the titration of \(O_3\) by NO produced \(NO_2\). The \(NO_2\) was carried over to the other places by air circulation, and/or oxidized to \(NO_3\) and \(N_2O_5\), which could further react with aerosol to form \(HNO_3\) and \(CINO_2\) in the evening. Horizontal and vertical transport dominated \(O_3\) sources, with the average positive contribution of 5.7±7.0 and 54.5±9.6 ppbv/hr during 16:00-08:00 LT on August 4-11, respectively. The strong vertical transport coincided with the downward winds in the evening, which might bring the high-altitude \(O_3\) to the ground, as indicated by Figure S9. However, the sources of \(O_3\) in the upper atmosphere were beyond the scope of this study.
Figure 7 Time series of O$_3$ variation rate in Ji’nan induced by individual processes calculated based on the change of O$_3$ per hour. Total transport is the sum of HTRA and VTRA, and the sum of O$_3$ variation rates attributable to all the processes is represented by total O$_3$ variation rate. The nighttime (18:00 – 06:00 LT) has been highlighted in grey.

### 3.4 Local O$_3$ formation and control

#### 3.4.1 Pathway and source contributions to O$_3$ production

Figure 8 shows the profiles of the six sources of O$_3$ precursors extracted from PMF. The first source contained high levels of $n/i$-pentanes and aromatics, likely representing gasoline exhaust (Ho et al., 2009; Ling and Guo, 2014). The heavy (C$_8$-C$_{10}$) hydrocarbons dominated in the second source accompanied by great abundances of the combustion tracers, such as C$_2$-C$_3$ hydrocarbons, CO, NO and NO$_2$, in line with the features of diesel exhaust (Liu et al., 2008). The third source was assigned as BVOC, due to the exclusively high loading of isoprene (Guenther, 2006). The fourth source was rich in C$_4$ hydrocarbons, including $n/i$-butanes and 1,3-butadiene. It was defined as liquefied petroleum gas (LPG) usage, since butanes and butenes are present in large quantities in China’s LPG (Song et al., 2008 and references therein). Solvent usage was represented by the fifth source, in view of the high loadings of hexane isomers (2,3-dimethylbutane, 2-methylpentane and 3-methylpentane) and moderate loadings of $n$-hexane, toluene, ethylbenzene and xylenes (Guo et al., 2011). At last, most of styrene, benzene, toluene, ethylbenzene and xylenes are allocated to the sixth source, which also contained moderate levels of light (C$_2$-C$_3$) hydrocarbons. Since styrene is a common petrochemical product (Jobson et al., 2004; Liu et al., 2008), this source was designated as petrochemical industry.
Figure 8 Profiles of the six sources of O$_3$ precursors in daytime of the VOC sampling days in Ji’nan.

Table 3 summarizes the percentage contributions of specific sources to O$_3$ precursors. Around a quarter (25.7±3.6%, referring to VOC mixing ratios and hereafter) of VOCs* was attributable to gasoline exhaust. Diesel exhaust, LPG usage, solvent usage and petrochemical industry made comparable (p>0.05) contributions to VOCs*, ranging from 14.7±2.0% to 18.8±3.1%. BVOC constituted the smallest part of VOCs*, accounting for 6.1±2.6%. Most (80-90%) of CO, NO and NO$_2$ were assigned to the exhausts from diesel and gasoline vehicles, particularly to diesel exhaust which was responsible for more than half of these trace gases.

Table 3 Contributions to VOCs, CO, NO, NO$_2$ and O$_3$ production rate by the sources of O$_3$ precursors averaged on the VOC sampling days in Ji’nan (Unit: % unless otherwise specified).

| Source       | VOCs* | CO   | NO   | NO$_2$ | O$_3$ production rate (ppbv/hr) |
|--------------|-------|------|------|--------|---------------------------------|
|              |       |      |      |        | O$_3$ episodes | Non-episodes |
| GE $^1$      | 25.7±3.6 | 29.9±2.1 | 30.9±2.4 | 22.2±2.4 | 1.8±0.6 | 1.0±0.3 |
| DE $^2$      | 17.6±2.4 | 57.3±5.2 | 52.0±5.8 | 54.4±5.8 | 1.7±0.4 | 1.0±0.3 |
| BVOC         | 6.1±2.6  | 0.0±1.7 | 0.0±2.8 | 0.0±2.3 | 1.2±0.5 | 0.2±0.1 |
| LPG $^3$     | 14.7±2.0 | 2.2±1.1 | 9.1±1.6 | 4.7±0.9 | 0.8±0.5 | 0.1±0.1 |
| Solvent $^4$ | 17.1±3.9 | 3.1±1.8 | 5.1±3.8 | 7.8±3.1 | 0.8±0.5 | 0.7±0.3 |
According to the process analysis by WRF-CMAQ, local photochemical formation was an important source of O₃ on episode days in Ji’nan, particularly during 09:00-15:00 LT when O₃ was at high levels (Figure 7). To investigate the local O₃ formation mechanisms, the PBM-MCM model was used to simulate the contributions of pathways and O₃ precursor sources to O₃ production. Table S4 lists the production and destruction pathways of O₃, which have been widely adopted in previous studies (Thornton et al., 2002; Monks, 2005; Kanaya et al., 2009).

Briefly, the oxidation of NO by HO₂ and RO₂ produced NO₂, which led to O₃ formation following NO₂ photolysis (R2 and R4-R5 in introduction). Therefore, the reactions between NO and HO₂/RO₂ were considered as the production pathways of O₃. To account for O₃ destruction, reaction between O²(D) and H₂O denoted the photolysis of O₃, and reactions of O₃ with OH, HO₂ and alkenes were also included. Furthermore, since the formation of HNO₃ through reaction of OH and NO₂ served as an important removal of NO₂, in addition to NO₂ photolysis which produced O₃ eventually, reaction between OH and NO₂ was treated to be destructive to O₃. The titration of O₃ by NO was not treated as an O₃ destruction pathway, because it produced NO₂ with the same amount of O₃ consumed. Though a fraction of NO₂ generated from the titration reaction could be removed by OH, leading to a net destruction of O₃ by NO titration, this was considered in the reaction between NO₂ and OH.

Figure 9 (a) and (b) show the 24 hour average simulated pathway contributions to O₃ production rate for the 6 O₃ episode days and 3 non-episode days. Also shown are the O₃ production rates simulated by PBM-MCM (O₃ production PBM-MCM), those explained by chemical reactions extracted from WRF-CMAQ simulation (O₃ production CHEM in WRF-CMAQ), and those calculated from the observed hourly O₃ (O₃ production obs.). Overall, O₃ production PBM-MCM and O₃ production obs. had the same magnitudes, especially during O₃ episodes with more stagnant weather conditions (section 3.2). This indicated that the PBM-MCM model reasonably reproduced the in situ O₃ photochemistry. O₃ production CHEM in WRF-CMAQ was generally lower than O₃ production PBM-MCM and O₃ production obs. However, the chemical O₃ productions simulated by WRF-CMAQ and PBM-MCM agreed well with each other during 10:00-15:00 LT on episode days, which might be explained by the dominant role of CHEM in O₃ sources in this period.
(Figure 7). The lower or even negative chemical contributions to O$_3$ productions simulated by WRF-CMAQ resulted from the titration of the regionally transported and/or local background O$_3$ by NO and the following depletion of NO$_2$ through reacting with OH and/or transport. Differently, PBM-MCM did not consider the transport of O$_3$, though the transport effect was partially represented by constraining the model to the observed concentrations of O$_3$ precursors. In addition, in contrast to the emission-based models (e.g., WRF-CMAQ), PBM-MCM was constructed by the observed air pollutants, which were already subject to chemical reactions before being detected by the analytical instruments. This meant that the reaction between NO and O$_3$ from the emission to the detection of NO$_x$ was not considered in PBM-MCM. However, as an emission-based model, WRF-CMAQ might perform better in describing the reactions immediately after the emissions of air pollutants. Therefore, the chemical destructions of O$_3$ in the vicinity of NO$_x$ sources might also account for the aforementioned discrepancy. The obviously higher reaction rate between NO and O$_3$ simulated by WRF-CMAQ (Figure S11) confirmed our inferences.

During both O$_3$ episodes and non-episodes, the reaction between HO$_2$ and NO dominated over “RO$_2$+NO” in O$_3$ production, while the O$_3$ destruction was mainly attributable to the formation of HNO$_3$ (OH+NO$_2$→HNO$_3$), the reaction between O$_3$ and HO$_2$ and photolysis of O$_3$, i.e. O$_3$(D)+H$_2$O. Note that the formation of nitric acid did not directly destroy O$_3$, but consumed NO$_2$ and consequently reduced O$_3$ production rate. The net O$_3$ production rate during O$_3$ episodes (maximum: 21.3 ppbv/hr) was much (p<0.05) higher than during non-episodes (maximum: 16.9 ppbv/hr), which partially explained the higher O$_3$ on episode days. In general, “OH+NO$_2$” serves as the chain terminating reaction in VOC-limited regime of O$_3$ formation, while the radical-radical reactions take over the role in NO$_x$-limited regime (Finlayson-Pitts and Pitts, 1993; Kleinman, 2005). Here, we found that the ratio of total reaction rates between “HO$_2$+RO$_2$” and “OH+NO$_2$” substantially increased from 0.2±0.1 during non-episodes to 1.0±0.3 during O$_3$ episodes (p<0.05). This suggested that O$_3$ formation during non-episodes was limited by VOCs, while it might switch to be co-limited by VOCs and NO$_x$ during episodes in view of the equivalent role of “HO$_2$+RO$_2$” and “OH+NO$_2$” in terminating the chain reactions.

Further, the 24 hour average contributions to net O$_3$ production rate of different sources of O$_3$ precursors were identified for the 6 episode days and 3 non-episode days, as presented in Figure...
The source contributions to the O\(_3\) production rate were obtained from the differences in simulated O\(_3\) production rates between a base run and a constrained run. In the base run, the O\(_3\) production rate was simulated with the observed concentrations of air pollutants except for the carbonyls, while the concentrations of air pollutants attributable to a specific source were deducted from the observed concentrations in the input of the constrained run. To account for the influence of primary hydrocarbons on the formation of carbonyls, and the subsequent impact on O\(_3\) production, carbonyls were not constrained to observations in either the base run or the constrained runs. However, the source-specific primary emissions of carbonyls and their contributions to O\(_3\) production were not considered in this approach. Therefore, the source-specific contributions to net O\(_3\) production rate were expected to be underestimated, as carbonyls are generally of high O\(_3\) formation potentials (Cheng et al., 2010; Dong et al., 2014).

The method was applied to each of the six sources, derived from the PMF analysis, thereby acquiring the contribution to O\(_3\) production rate of each source.

On average, the source contributions (in ppbv/hr) to O\(_3\) production rates during O\(_3\) episodes and non-episodes are presented in Table 3. It was found that gasoline exhaust and diesel exhaust were the largest contributors to O\(_3\) production regardless of O\(_3\) episodes or non-episodes. Specifically, the net O\(_3\) production rate was 1.0±0.3 ppbv/hr for both gasoline and diesel exhaust during non-episodes, which however increased to 1.8±0.6 ppbv/hr for gasoline exhaust and 1.7±0.4 ppbv/hr for diesel exhaust during O\(_3\) episodes. This suggested that vehicular emissions played critical roles in building up ground-level O\(_3\) in Ji’nan. If carbonyls were taken into account, the contributions of vehicular emissions to O\(_3\) production rate were even higher than the currently simulated values, due to the dominance of vehicular exhausts in the sources of carbonyls in urban areas (Grosjean et al., 1990; Granby et al., 1997). In addition, the contributions of the other sources to O\(_3\) production rates all increased during O\(_3\) episodes except for solvent usage (p>0.05), as listed in Table 3. It is not surprising to see the coincident increases, in view of the higher simulated and observed overall O\(_3\) production rate during episodes. Further insight into the percentage contributions (not shown here) found that the contributions of BVOC, LPG usage and petrochemical industry relative to the sum of the O\(_3\) production rates of the 6 sources increased substantially from 9.9±4.2%, 4.3±1.4% and -2.8±1.9% during non-episodes to 19.2±4.3%, 9.1±3.4% and 12.1±3.1% during O\(_3\) episodes, respectively. The increased O\(_3\) production rates by BVOCs could be explained by the increase of isoprene (episodes: 2.2±0.6
ppbv; non-episodes: 0.9±0.3 ppbv), under higher temperature and stronger solar radiation during O$_3$ episodes. The enhanced O$_3$ formation from petrochemical industry on episode days was likely associated with the dominance of continental air (Figure 4) and the extensive petrochemical industries in the NCP, elevating the concentrations of photochemical VOCs. For example, the observed mixing ratio of styrene increased from 54.7±22.0 pptv during non-episodes to 162.3±44.7 pptv during O$_3$ episodes. The reason for elevated O$_3$ production rate by LPG usage during episodes was unknown. It is worth noting that the source contributions to O$_3$ production might have some uncertainty due to the limited number of samples (54 samples) and O$_3$ precursors (31 VOCs, CO, NO and NO$_2$) for source apportionment.

Figure 9 Pathway contributions to O$_3$ production and destruction rate during episodes (a) and non-episodes (b). Contributions of O$_3$ precursor sources to net O$_3$ production rate during episodes (c) and non-episodes (d).

3.4.2 O$_3$ control measures
As the tropospheric O₃ is produced through the reactions between VOCs and NOₓ, the relationships between O₃ and the precursors were investigated. Since WRF-CMAQ simulated the highest contribution of chemical reactions to O₃ production rate at 9:00-15:00 LT and the PBM-MCM indicated the maximum O₃ production rate at 12:00 LT, the isopleths of the net O₃ production rate at 12:00 LT are plotted in Figure 10, as a function of the OH reactivity of VOCs (\(OH\text{ reactivity}_{\text{VOCs}}\)) and NOₓ (\(OH\text{ reactivity}_{\text{NOx}}\)). The OH reactivity instead of the absolute concentrations was plotted, because we intended to show the reactivity-dependent reductions of source emissions, as discussed later. It is noteworthy that the OH reactivity was calculated as the products of the observed concentrations of O₃ precursors and the corresponding reaction rate constants between O₃ precursors and OH, rather than observed or modeled values. 

\(OH\text{ reactivity}_{\text{VOCs}}\) in Figure 10 are the percentages relative to the average \(OH\text{ reactivity}_{\text{VOCs}}\) during O₃ episodes of the VOC sampling days, the same for \(OH\text{ reactivity}_{\text{NOx}}\). The scenario with both \(OH\text{ reactivity}_{\text{VOCs}}\) and \(OH\text{ reactivity}_{\text{NOx}}\) equaling 100% represents the average \(OH\text{ reactivity}_{\text{VOCs}}\) and \(OH\text{ reactivity}_{\text{NOx}}\) during O₃ episodes, respectively. The \(OH\text{ reactivity}_{\text{VOCs}}\) throughout the VOC sampling period were within the range of 33-123% of the average \(OH\text{ reactivity}_{\text{VOCs}}\) during O₃ episodes. For \(OH\text{ reactivity}_{\text{NOx}}\), the range was 61-242%. To include the OH reactivity of VOCs and NOₓ on all the VOC sampling days, factors from 10% to 140% with the step of 10% were applied to the average diurnal profiles of VOCs and CO during O₃ episodes, while the factors ranged from 10% to 300% with the step of 10% for NOₓ. For example, when the average VOCs and NOₓ during O₃ episodes were multiplied by a factor of 50% and 120%, respectively, \(OH\text{ reactivity}_{\text{VOCs}}\) and \(OH\text{ reactivity}_{\text{NOx}}\) in this scenario were 50% and 120% of those averaged over O₃ episodes, respectively. The initial concentrations of all air pollutants were also scaled by these same factors and the model was constrained to these scaled concentrations every hour, except for O₃, which was not a model input. It should be noted that the factors applied to CO were exactly the same as those applied to VOCs, therefore we use VOCs\(^*\) to represent the sum of VOCs and CO hereafter. The 14 gradients of \(OH\text{ reactivity}_{\text{VOCs}}\)\(^*\) and 30 gradients of \(OH\text{ reactivity}_{\text{NOx}}\) made up 420 scenarios, thus the isopleths were made with 420 simulated O₃ production rates at 12:00 LT. Meteorological conditions were exactly the same for all the scenarios and the clear sky was hypothesized.
As shown in Figure 10, O$_3$ formation can be divided into VOC$^\#$-limited regime and NO$_x$-limited regime with the method used in Lyu et al. (2017). Briefly, at a given $OH$ reactivity$_{VOC^\#}$, O$_3$ production rate generally reached the maximum at a specific $OH$ reactivity$_{NOX}$ due to the dual role of NO$_x$ in O$_3$ formation. The scenario with this specific $OH$ reactivity$_{NOX}$ was treated as dividing point between NO$_x$-limited regime and VOC$^\#$-limited regime. Since 14 gradients of $OH$ reactivity$_{VOC^\#}$ (10% - 140% with the step of 10%) were set for all the scenarios, 14 pairs of $OH$ reactivity$_{NOX}$ and $OH$ reactivity$_{VOC^\#}$ were obtained, as shown by the orange crosses in Figure 10. A dividing line was acquired from the linear regression between $OH$ reactivity$_{VOC^\#}$ and $OH$ reactivity$_{NOX}$ in these scenarios (orange dashed line in Figure 10). O$_3$ formation was limited by VOCs$^\#$ and NO$_x$ in the lower right and upper left of the dividing line, respectively. Since the horizontal and vertical coordinates were percentages relative to the average $OH$ reactivity, we did not present the dividing ratio of $\frac{OH$ reactivity$_{VOC^\#}}{OH$ reactivity$_{NOX}}$ here. Further, it was found that O$_3$ production rate was also enhanced with the increase of $OH$ reactivity$_{VOC^\#}$ in the upper left area close to the dividing line. We defined it as a transition area where the O$_3$ production rate was comparably sensitive to VOCs$^\#$ and NO$_x$. Beyond the transition area in the upper left of the dividing line, the sensitivity of O$_3$ production rate to NO$_x$ was generally ten times higher than to VOCs$^\#$, which was designated as NO$_x$-limited regime. The transition area and the NO$_x$-limited regime are divided by the blue dashed line in Figure 10.

Based on these sensitivity simulations, it was found that O$_3$ formation was mainly limited by VOCs$^\#$ during non-episodes. However, it switched to be co-limited by VOCs$^\#$ and NO$_x$ (transition regime) on episode days with the net O$_3$ production rate among the highest, except for August 5 when the strong sea breeze might dilute air pollutants in Ji’nan and/or intercept the transport of air pollutants from Central China to Ji’nan (Figure S6). Theoretically, it was also possible that O$_3$ formation was limited by NO$_x$ during episodes, in view of the overestimation of NO$_2$ by the chemiluminescence analyzer which was expected to be more significant than during non-episodes. However, O$_3$ formation was not likely only limited by NO$_x$, which should be still sensitive to VOCs, as NO$_2$ could not be much overestimated in the urban areas (see section 2.2.1). Therefore, O$_3$ formation was considered to be in the transition regime during episodes. This might partially explain the increased O$_3$ during episodes in Ji’nan, given the higher O$_3$
production rates in transition area (Figure 10). Noticeably, this trend is also consistent with the regime change predicted by the \( \frac{OH \text{ reactivity}_{\text{VOCs}^s}}{OH \text{ reactivity}_{\text{NOx}}} \) presented in section 3.1.

Furthermore, since \( \text{O}_3 \) formation during episodes was generally co-limited by \( \text{VOCs}^s \) and \( \text{NOx} \) or even more limited by \( \text{NOx} \) considering the overestimation of \( \text{NO}_2 \), it was expected that reducing emissions of either \( \text{VOCs}^s \) or \( \text{NOx} \) would alleviate \( \text{O}_3 \) pollution on high \( \text{O}_3 \) days. However, the decrease of \( \text{NOx} \) would enhance \( \text{O}_3 \) production during non-episodes. This meant that a compromise should be made between the reduction of average \( \text{O}_3 \) (during non-episodes) and highest \( \text{O}_3 \) (during episodes) when the \( \text{O}_3 \) control measures mainly focused on \( \text{NOx} \) in Ji’nan. The effects of emission restrictions of \( \text{O}_3 \) precursors from specific sources, as indicated by PMF analysis, on \( OH \text{ reactivity}_{\text{VOCs}^s} \) and \( OH \text{ reactivity}_{\text{NOx}} \) are presented in Figure 10 (straight solid lines #1-#6). The start point of the straight lines corresponded to 100% of \( OH \text{ reactivity}_{\text{VOCs}^s} \) and \( OH \text{ reactivity}_{\text{NOx}} \), namely the average condition during \( \text{O}_3 \) episodes. The end points, however, denote \( OH \text{ reactivity}_{\text{VOCs}^s} \) and \( OH \text{ reactivity}_{\text{NOx}} \) in the atmosphere when the specific source emissions are removed. Therefore, the length of the lines reflects the potential of each PMF-derived \( \text{O}_3 \) precursor source to alter \( OH \text{ reactivity}_{\text{VOCs}^s} \) and \( OH \text{ reactivity}_{\text{NOx}} \) in the atmosphere. Clearly, diesel and gasoline exhausts were the sources significantly contributing to the \( OH \text{ reactivity}_{\text{VOCs}^s} \) and \( OH \text{ reactivity}_{\text{NOx}} \) during \( \text{O}_3 \) episodes. Emission restriction of vehicle exhausts during \( \text{O}_3 \) episodes would greatly benefit \( \text{O}_3 \) reduction in Ji’nan. Figure S12 shows the simulated \( \text{O}_3 \) production rate as a function of the source emission reduction, which also confirmed the highest efficiencies of \( \text{O}_3 \) reduction by cutting diesel exhaust (0.58 ppbv-h\(^{-1}\)/10% emission reduction) and gasoline exhaust (0.47 ppbv-h\(^{-1}\)/10% emission reduction). We also found that the reduction of diesel exhaust would lead to the increase of \( \text{O}_3 \) production rate when the reduction percentages were lower than a dividing point (e.g., 60% on August 10), while further reductions would decrease the \( \text{O}_3 \) production rate. This was due to high emission of \( \text{NOx} \) from diesel vehicles and dual roles of \( \text{NOx} \) in \( \text{O}_3 \) formation. However, the enhancement of \( \text{O}_3 \) production rate was very minor (<0.1 ppbv/hr), as the \( \text{O}_3 \) formation during episodes was in the transition area. In fact, constraint on diesel exhaust would progressively shift \( \text{O}_3 \) formation to a \( \text{NOx} \)-limited regime where cutting \( \text{NOx} \) would be quite effective for \( \text{O}_3 \) control (red line in Figure 10). Therefore, constraints of vehicle emissions are most effective on \( \text{O}_3 \) abatement in Ji’nan. It is noteworthy that \( \text{VOCs}^s \) and \( \text{NOx} \) (if any) in all the sources were cut in
the same proportions, which was generally the most feasible emission reduction scheme. The situations might change when VOCs and NOx emissions were cut by different proportions.

Figure 10 Isopleths of the net O3 production rate (ppbv/hr) at 12:00 LT as a function of OH \( \text{reactivity}_{\text{VOCs}}^* \) and OH \( \text{reactivity}_{\text{NOx}} \). The red blocks and orange circles denote the calculated OH \( \text{reactivity}_{\text{VOCs}}^* \) and OH \( \text{reactivity}_{\text{NOx}} \) at 12:00 LT on O3 episode and non-episode days, respectively. Each orange cross represents the OH \( \text{reactivity}_{\text{VOCs}}^* \) at 12:00 LT in the scenario with highest O3 production rate at a given OH \( \text{reactivity}_{\text{NOx}} \). The orange dashed line and blue dashed line divide O3 formation into the VOC-limited regime, transition area, and NOx-limited regime.

4 Implications

This study investigates the causes of a severe O3 pollution event lasting for eight consecutive days in the NCP, one of the most densely populated regions in the world. Photochemical O3 formation in the lower troposphere of the NCP is demonstrated as the main source, under the synoptic conditions of weak high pressure or low pressure trough. Though NOx, as an important precursor of O3, has been significantly reduced in emissions in China since 2011 (Duncan et al., 2016; Liu et al., 2017), O3 pollution is still severe or even becoming worse in the NCP, as...
revealed in the present and also previous studies (Zhang et al., 2014; Sun et al., 2016). The finding that O₃ formation shifted from VOC-limited regime on relatively low O₃ days to the transition area on O₃-unattainment days may elucidate the cause of the increase in O₃, because O₃ productions in the transition area are even higher, despite decreases in NOₓ emissions. Consistent with previous studies, the NCP is identified as a source region of O₃ in this study. It can be expected that organic nitrates are also intensively formed as byproducts in the photochemical cycles of O₃ formation. In combination with the fact that the NCP locates within the mid-latitude band of Northern Hemisphere under the dominance of westerlies, O₃ and organic nitrates formed in this region can be transported over a long distance following uplift processes, which has been confirmed to partially account for the enhancement of background O₃ in North America and even Europe (Derwent et al., 2015; Lin et al., 2017). Taking into consideration the high O₃ levels and their upward trend in the NCP, it is not realistic to believe that the reduction of NOₓ in China will ease the global O₃ burden in a short period. More stringent control measures may be needed to achieve an O₃ benefit, with comprehensive thinking of atmospheric dynamics and chemistry.

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