Causes of ozone pollution in summer in Wuhan, Central China

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Abstract

In August 2016, continuous measurements of volatile organic compounds (VOCs) and trace gases were conducted at an urban site in Wuhan. Four high-ozone (O3) days and twenty-seven non-high-O3 days were identified according to the China’s National Standard Level II (~100 ppbv). The occurrence of high-O3 days was accompanied by tropical cyclones. Much higher concentrations of VOCs and carbon monoxide (CO) were observed on the high-O3 days (p < 0.01). Model simulations revealed that vehicle exhausts were the dominant sources of VOCs, contributing 45.4 ± 5.2% and 37.3 ± 2.9% during high-O3 and non-high-O3 days, respectively. Both vehicle exhausts and stationary combustion made significantly larger contributions to O3 production on high-O3 days (p < 0.01). Analysis using a chemical transport model found that local photochemical formation accounted for 74.7 ± 5.8% of the daytime O3, around twice the regional transport (32.2 ± 5.4%), while the nighttime O3 was mainly attributable to regional transport (59.1 ± 9.5%). The local O3 formation was generally limited by VOCs in urban Wuhan. To effectively control O3 pollution, the reduction ratio of VOCs to NOx concentrations should not be lower than 0.73, and the most efficient O3 abatement could be achieved by reducing VOCs from vehicle exhausts. This study contributes to the worldwide database of O3-VOC-NOx sensitivity research. Its findings will be helpful in formulating and implementing emission control strategies for dealing with O3 pollution in Wuhan.

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1. Introduction

Over the past decades, tropospheric ozone (O3) pollution has become a major problem around the world because of its deleterious impact on human health, vegetation, and climate (Krupa and Manning, 1988; Tilton, 1989; Stevenson et al., 2013; Monks et al., 2015). In recent years, the issue of severe O3 pollution in megacities and fast-developing regions in China has attracted much attention (Wang et al., 2009; Xue et al., 2014; Verstraeten et al., 2015; Gao et al., 2017a, 2017b; Wang et al., 2017). To effectively control O3 pollution, it is essential to understand the characteristics and formation mechanisms of O3 pollution in Chinese cities with different energy structures and geographic features, such as Wuhan in Central China.

The global background, intrusion of stratospheric O3, and photochemical formation are the main sources of tropospheric O3, among which photochemical formation generally dominates O3 levels in urban areas (Monks et al., 2015; Wang et al., 2016; Gao et al., 2017a, 2017b; Wang et al., 2017). In ozone chemistry, O3 is formed through the combination of an oxygen atom from NO2 photolysis with oxygen (O2) (Logan, 1985; Roelofs and Lelieveld, 1997). Conversely, O3 reacts with NO, regenerating NO2. NO, NO2, and O3 can reach a photo-equilibrium, which is driven by oxidative radicals (e.g. OH, HO2, and RO2) (Monks, 2005). NOx plays a dual role in O3 formation. In a low NOx environment, it stimulates O3 formation, while in a NOx-rich environment, O3 is depleted by NOx mainly due to the titration of NO to O3 (Wang et al., 2016). The relationship between O3 and its precursors in these complicated photochemical processes have been well documented in many previous studies. For example, it has been extensively reported that...
VOCs are the limiting factors of \( O_3 \) production in the urban areas of many Chinese cities, from Beijing in the north to Hong Kong in the south (Wang et al., 2010; Lyu et al., 2016b; Xu et al., 2017). However, in rural or background regions, \( O_3 \) formation is generally \( \text{NO}_x \)-limited due to the relatively low \( \text{NO}_x \) (high VOCs/\( \text{NO}_x \) ratio) in the atmosphere (Pan et al., 2015; Xu et al., 2015). A \( \text{NO}_x \)-limited regime has also been observed or simulated in some cities of western China (Xue et al., 2014; Feng et al., 2016). Regardless of the regimes controlling \( O_3 \) formation, the responses of \( O_3 \) formation to precursors are generally non-linear, as has been revealed by empirical kinetic modeling approach (EKMA) curves (Lin et al., 1988; Jia et al., 2016; Lyu et al., 2016a). In a \( O_3 \)-limited regime, alkenes, aromatics, and biogenic VOCs have been repeatedly confirmed as the main contributors to \( O_3 \) production. An et al. (2012) indicated that aromatics and alkenes contributed 73–84% to \( O_3 \) production in summer 2008 in Beijing. Han et al. (2013) found that alkenes were the largest contributors to \( O_3 \) production (53.3%), followed by aromatics (35.1%) and alkanes (9.2%), in autumn 2009 in Tianjin. Geng et al. (2007) reported that aromatics were the main contributor (79%) to \( O_3 \) production in November 2005 in Shanghai. The sources of VOCs in China have also been widely investigated (Guo et al., 2007; Yuan et al., 2010; Lyu et al., 2016b; Guo et al., 2017a, 2017b). The contributions of different sources to VOCs vary significantly among cities and regions, but vehicular and industrial emissions are generally the predominant sources of ambient VOCs in China (see Table S1 for details). For instance, Shao et al. (2016) indicated that in summer 2013 in Nanjing, industry-related sources (52%) were the largest contributor to VOCs, followed by vehicular emissions (34%). Yuan et al. (2009) reported that vehicular emissions made the largest contribution to ambient VOCs at both urban (62%) and rural sites (36%) in 2006 in Beijing. Ling and Guo (2014) found that vehicular-related sources, including gasoline exhaust (22%), diesel exhaust (26%), LPG usage (21%), and gasoline evaporation (8%), were the dominant contributors to VOCs in autumn 2010 in Hong Kong.

Wuhan is the largest city in Central China; it is located in an area dominated by the moist subtropical monsoon climate. Due to rapid industrialization and urbanization, \( O_3 \) pollution has become increasingly severe in Wuhan. Ozone was identified as the main air pollutant on 44 days in 2015 and on 34 days in 2016 in Wuhan, when the \( O_3 \) un-attainment rate was 15.7% and 9.3% according to China’s National Ambient Air Quality Standard Level II (200 \( \mu \)g m\(^{-3}\)), respectively (accessible at http://www.whepb.gov.cn/hbbhjzkgb/19431.html). Higher \( O_3 \) values were generally observed in summer, with a peak concentration of 121 ppbv in 2015 and 116 ppbv in 2016. As such, Wuhan faces major challenges in \( O_3 \) abatement, like other fast-developing cities and regions in China.

This study aims to characterize \( O_3 \) pollution during high-\( O_3 \) and non-high-\( O_3 \) days so as to understand the main causes of high \( O_3 \) days in Wuhan. The concentrations and compositions of VOCs and \( \text{NO}_x \) are first compared between high-\( O_3 \) and non-high-\( O_3 \) days. Next, a positive matrix factorization (PMF) receptor model coupled with a photochemical box model incorporating the Master Chemical Mechanism (PBMM-CMM) is applied to investigate the major sources and their contributions to ambient VOCs and photochemical \( O_3 \) formation during high-\( O_3 \) days and non-high-\( O_3 \) days. Finally, \( O_3 \)-precursor relationships are evaluated using a relative incremental reactivity (RIR) approach, and a reduction ratio of VOCs/\( \text{NO}_x \) is recommended for effective mitigation of \( O_3 \) pollution in Wuhan. The outcomes are expected to improve our understanding of photochemical \( O_3 \) formation and transport mechanisms for subtropical regions that have moist monsoon climates and a complex coupling of meteorology and chemistry. Our results also have implications for other subtropical inland regions around the world.

2. Methodology

2.1. Sampling site

The sampling site is located in the urban area of Wuhan (30.604° N, 114.278° E), which is adjacent (~70 m) to a main traffic road and surrounded by residential and commercial blocks (Fig. 1). The instruments were deployed on the roof of a nine-story building (~25 m a.g.l.), the Wuhan Research Institute of Environmental Protection.

2.2. Measurement techniques

2.2.1. Online measurement of ambient VOCs

102 VOCs species, including 58 non-methane hydrocarbons (NMHCs), 31 halocarbons, and 13 oxygenated VOCs (OVOCs), were analyzed using an online gas chromatography-mass spectrometry-flame ionization detector system with 1-h time resolution (GC-MSD-FID, TH-PKU 300B; Tianhong Instrument Co., Ltd., Wuhan). This online system has four parts: the sampling system, pre-concentrator, GC-MSD-FID system, and data processing system. Ambient air was continuously drawn through a Teflon tube with an inner diameter of 0.76 cm, and a particle filter was connected to the sampling tube inlet to remove ambient particles. The sampling tube inlet was installed at 1–2 m above the rooftop, and the outlet was connected to a PFA-made manifold with a bypass pump drawing air at a rate of 15 L min\(^{-1}\). Air samples were collected and transferred to the pre-concentrator; water and carbon dioxide were removed at ~80 °C and VOCs were trapped at ~150 °C. After preconcentration, the VOCs were desorbed by rapidly heating up the trap to 100 °C, and then introduced into the GC-FID-MSD system (Li et al., 2015; Lyu et al., 2016). The C2 – C4 NMHCs were analyzed by the FID, while other compounds were quantified by MSD. The quality assurance and control (QA/QC) are shown in Text S1.

2.2.2. Monitoring of trace gases other than VOCs and meteorological parameters

Five trace gases (\( O_3 \), \( \text{NO}_2 \), \( NO \), \( CO \), and \( \text{SO}_2 \)) were measured continuously from August 1 to 31, 2016, with a 1-h resolution. Trace gases were monitored using instruments developed by Thermo Environmental Instruments (TEI) Inc. Specifically, \( O_3 \) was detected with a commercial UV photometric analyzer (TEI, Model 49i), which has a detection limit of 1.0 ppbv. Nitric oxide (NO) and \( \text{NO}_2 \) were analyzed by a chemiluminescence trace level analyzer (TEI, Model 42i) with a detection limit of 0.5 ppbv (Geng et al., 2009). A gas filter correlation CO analyzer (TEI, Model 48i) was used to detect ambient CO. The detection limit of the CO analyzer was 0.04 ppm. Sulfur dioxide (\( \text{SO}_2 \)) was analyzed using a pulse fluorescence analyzer (TEI, Model 43i) with a detection limit of 0.05 ppbv. The QA/QC of trace gases can be found in Text S1. Weather parameters, including temperature, relative humidity, pressure, wind speed, and wind direction, were also monitored at the site with a 1-h resolution by the integrated sensor suite (Vantage Pro TM & Vantage Pro 2 Plus TM Weather Stations, Davis Instruments).

In this study, high-\( O_3 \) days were defined as those when the highest hourly \( O_3 \) concentration exceeded China’s National Ambient Air Quality Standard Level II of 200 \( \mu \)g m\(^{-3}\) (~100 ppbv) (accessible at http://english.mep.gov.cn/Resources/standards/Air_Environment/quality_standard1/201605/20160511_337502.shtml). Otherwise, the sampling days were denoted as non-high-\( O_3 \) days. As such, four high-\( O_3 \) days (August 1, 17, 24, and 30) were captured during the entire sampling period.
2.3. Model description

2.3.1. PMF model

The U.S. Environmental Protection Agency (EPA) Positive Matrix Factorization (PMF, version 5.0) model was applied to identify the sources of ambient VOCs and to quantify their contributions to VOCs. PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices: factor contributions (G) and factor profiles (F). Here, “factor contribution” means the contribution of a source to the total measured VOC concentration in a sample, while “factor profile” indicates the percentages of individual VOC species in the total measured VOC concentration in a sample. To ascribe the concentrations of chemical species in n samples to p independent sources, the receptor model can be generally expressed as follows (Eq. (1)):

\[ x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \]  

(1)

where \( x_{ij} \) (unit: ppbv) is the concentration of the jth species in the ith sample, \( g_{ik} \) (unit: ppbv) is the contribution of the kth source to the ith sample, \( f_{kj} \) is the fraction of jth species in kth source, and \( e_{ij} \) is the residual for the ith sample of the jth species.

The factor profiles were derived based on the principle that the objective function Q should have the lowest value, as shown in Eq. (2) \((\text{Paatero and Tapper, 1994; Paatero, 1997})\). In addition, the profiles should have the best interpretability.

\[ Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{e_{ij}}{u_{ij}} \right)^2 \]  

(2)

where \( u_{ij} \) is the uncertainty of the ith species in the jth sample. The function value, \( Q(\text{robust}) \), was calculated using the model by excluding the points with uncertainty-scaled residuals greater than 4. The profile with the lowest value of \( Q(\text{robust}) \) was selected as the optimum solution.

In this study, speciated VOCs including 20 NMHCs, chloro-methane, and trichloroethylene from 565 samples were input into the PMF model. The 22 species were selected because most of them are tracers of different sources. Because accuracies in measurements for all species were <10% (Text S1), we used 10% as input to represent the uncertainty of each species in each sample in the model. Different numbers of factors were tested, and an optimum solution was determined based on good fit to the observed data and the most meaningful results. Eventually, seven factors were extracted from the PMF model simulation.

2.3.2. PBM-MCM model

A zero-dimension Lagrangian photochemical box model incorporating a Master Chemical Mechanism (PBM-MCM) was applied to investigate in situ photochemical \( \text{O}_3 \) formation in Wuhan in August 2016. This model simulates the complex photochemistry within a well-mixed boundary layer air parcel, including 5900 species and 16,500 reactions. All air pollutants were assumed to be well mixed in the atmospheric boundary layer defined by the model. It should be noted that vertical and horizontal dispersions were not considered in the model. This model was described in detail by Lam et al. (2013) and its reliability has been repeatedly confirmed in previous studies (Cheng et al., 2013; Guo et al., 2013; Ling et al., 2014; Lyu et al., 2016b). In this study, the observed hourly values of 52 VOCs and four trace gases (NO\(_2\), NO, SO\(_2\), and CO), in addition to temperature and relative humidity, between 00:00 local standard time (LST) and 23:00 LST were used to construct the model. The photolysis rates of different chemicals in the model were parameterized using the photon flux determined from the Tropospheric Ultraviolet and Visible Radiation (TUVv5) model (Lam et al., 2013). The simulations of daytime hours (07:00—19:00 LST) were conducted for the entire sampling period except for the rainy days, and the model output was the simulated hourly mixing ratios of \( \text{O}_3 \). The in situ \( \text{O}_3 \) production, the \( \text{O}_3-\text{NO}_x-\text{VOCs} \) relationship, and

Fig. 1. Geographical location of the sampling site.
the control strategies of O3 were all simulated using the PBM-MCM model. Details of the modeling results are shown in section 3.2.2 and section 3.4.

In addition to the simulation of O3 production, the PBM-MCM model was applied to investigate O3–precursor relationships by examining the relative incremental reactivity (RIR) of O3 precursors. The RIR is the percentage change in daytime O3 production per percent change in precursor. O3 precursors were divided into four groups: anthropogenic VOCs (AVOCs), BVOCs, CO, and NOx. A positive RIR for a given precursor means that reducing emissions of this precursor will significantly reduce O3 production, whereas a negative RIR indicates the opposite effect, i.e., cutting emissions of the precursor will enhance O3 production. In general, the RIRs of VOCs are positive, while both positive and negative RIRs are commonly seen for NOx due to its dual role in O3 chemistry. The VOC-limited (VOC-sensitive) regime is indicated by the positive RIRs of VOCs and negative RIRs of NOx. Otherwise, O3 formation is limited by (sensitive to) NOx or both VOCs and NOx when the RIR of NOx is positive.

The RIR for precursor X at site “s” is calculated using Eq. (3) (Cardelino and Chameides, 1995):

$$RIR_i^s(X) = \frac{P_{O_3,NO}^s(X) - P_{O_3,NO}^s(X - \Delta X)}{P_{O_3,NO}^s(X)}$$

where X represents a specific precursor (i.e., VOCs, NOx, or CO); the superscript “s” is used to denote the specific site where the measurements were made; S(X) is the measured mixing ratio of species X (ppbv); ΔS(X) is the hypothetical change in the mixing ratio of X, which is artificially set at 10%; P_{O_3,NO}^s(X) represents the simulated O3 production in the base run constructed with the observed concentrations of all O3 precursors, including species X. P_{O_3,NO}^s(X - \Delta X) is the simulated O3 production in the constrained run with 10% reduction of species X (Ling et al., 2013; Wang et al., 2018; Xu et al., 2017); while the concentrations of other species remain unchanged. The titration of O3 by NO was considered in both runs. Then, the average RIR value (RIR) for the species X over multiple sampling days was calculated using Eq. (4), where NS means the number of days simulated.

$$RIR = \frac{\sum_{1}^{NS} RIR_i^s(X) P_{O_3,NO}^s(X)}{\sum_{1}^{NS} P_{O_3,NO}^s(X)}$$

2.3.3. WRF-CMAQ model

The U.S. EPA Community Multiscale Air Quality (CMAQ) model with the Carbon Bond 05 (CB05) chemical mechanism was applied to simulate O3 concentrations during high-O3 days. CMAQ is a three-dimensional atmospheric chemistry and transport modeling system; more details can be found at http://cmascenter.org/cmaq/. In this study, CMAQ was driven by the meteorological fields from the Weather Research and Forecasting (WRF) model, which is one of the most commonly used models for both forecasting and atmospheric research across scales ranging from meters to thousands of kilometers. The simulation period was 00:00 LST, August 13, 2016, to 23:00 LST, August 18, 2016, when continuously high O3 values were observed, with the highest hourly O3 of 133.9 ppbv on August 17 (Fig. S1). The purpose of running the model simulations for six consecutive days was to ensure that the modeling could achieve a balance of intermediates (e.g., radicals) and reduce integration error in numerical calculations (Jiang et al., 2008; Pan et al., 2015; Chen et al., 2018). Two nested domains were defined in the WRF modeling, and the corresponding grid spacings were 27 km and 9 km, respectively. The outer domain (DM1, 27 km) covered most of China, and the second domain (DM2, 9 km) included most cities in eastern Hubei Province, and some parts of Anhui, Henan, and Jiangxi Provinces. Vertically, there were 31 sigma levels, with fixed at 100 hPa. The meteorological parameters were well considered by the model (Jiang et al., 2010). The anthropogenic emission inventory developed by Tsinghua University based on figures for 2010 was applied for this study, which includes monthly anthropogenic emissions of SO2, NOx, CO, ammonia (NH3), PM2.5, PM10, black carbon (BC), organic carbon (OC), and non-methane volatile organic compounds (NMVOCs). The data have a horizontal resolution of 0.25° × 0.25°. More details are given by He (2012). The biogenic emissions were calculated offline using the Model of Emissions of Gases and Aerosols from Nature (MEGAN, version 2.04) (Guenther et al., 2006). These modeling systems have been successfully used in previous O3 simulations by Jiang et al. (2010) and Wang et al. (2015).

3. Results and discussion

3.1. Characteristics of meteorological parameters and air pollutants

Table S2 shows the descriptive statistics of meteorological parameters on high-O3 and non-high-O3 days. The occurrence of high-O3 days was associated with high temperature, low wind speed, and low relative humidity. Fig. S3 presents the distributions of mean sea level (MSL) pressure and wind fields averaged over high-O3 days and non-high-O3 days in East Asia. It is shown that the high-O3 days were all related to tropical cyclones. This relation exists because Wuhan is located on the periphery of tropical cyclones, where relatively high pressure and subsiding air are formed, causing O3 accumulation. In addition, east to north winds induced by the tropical cyclones also brought polluted air masses from East China and North China to Wuhan on these days. A detailed discussion is given in Text S2 in the Supplement.

The time series of observed O3 concentrations in Wuhan in August 2016 is shown in Fig. S1. Based on the definition of a high-O3 day, August 1, 17, 24, and 30 were defined as high-O3 days during the sampling period. Table S3 shows the statistical descriptions of air pollutants on high-O3 and non-high-O3 days. During high-O3 days, the O3 mixing ratio was 61.2 ± 4.4 ppbv, about 40% higher than on non-high-O3 days (42.3 ± 2.0 ppbv; p < 0.01). The mixing ratios of O3 precursors, i.e., CO and total VOCs (TVOCs) representing the sum of mixing ratios of 102 VOC species, were 987.8 ± 95.4 and 43.9 ± 3.8 ppbv on high-O3 days, respectively, about 37% and 33% higher than on non-high-O3 days (p < 0.01). However, the levels of NO and NO2 were comparable between high-O3 and non-high-O3 days (the differences <2 ppbw, p>0.05). Previous studies indicated that O3 formation is generally limited by VOCs and suppressed by NOx in urban areas (Wang et al., 2008; Ling et al., 2013; Liu et al., 2016b). Hence, the more abundant TVOCs and CO during high-O3 days and comparable NOx values between high-O3 and non-high-O3 days might indicate the significant contribution of local photochemical reactions to O3 formation.

Fig. S2 shows the diurnal variations of O3, NOx, and m,p-xylene/ethylbenzene ratio on high-O3 and non-high-O3 days. The observed O3 generally peaked in the afternoon, and had relatively low concentrations from midnight to the early morning on both high-O3 and non-high-O3 days. A trough of O3 appeared at about 08:00 LST, which was likely caused by enhanced NO titration due to increased vehicular emissions of NO during morning rush hour (So and Wang,
In fact, the diurnal variation of NOx was opposite to that of O3: high levels of NOx appeared in the morning and evening when O3 was relatively low, and the increase of O3 from 09:00 to 15:00 corresponded to the decrease of NOx. The opposite diurnal patterns between O3 and NOx indicated that O3 formation in Wuhan was in a VOC-limited (NOx-suppressed) regime. The diurnal trend of m,p-xylene/ethylbenzene was also negatively correlated to O3. Because m,p-xylene is more reactive than ethylbenzene, the ratios of m,p-xylene/ethylbenzene decreased when photochemical reaction occurred. Indeed, the lowest ratios were observed in early afternoon when O3 peaked, while higher ratios were found in the morning and late afternoon, indicating fresh vehicular exhaust emissions and relatively weak photochemical consumption of VOCs.

Fig. 2 shows the diurnal variations of TVOCs, ethene, propane, toluene, and isoprene on O3 and non-high-O3 days. In general, the patterns between high-O3 and non-high-O3 days for TVOCs and individual VOC species were similar, except for the magnitude. Moreover, TVOCs showed the same trend as ethene, propane, and toluene: a bimodal structure was observed with the first peak in the morning and the second one in late afternoon, likely due to vehicular exhausts during rush hour and strong photochemical reactions at noon and in early afternoon. Clearly, the mixing ratios of TVOCs, ethene, propane, and toluene during high-O3 days were about 37%, 31%, 48%, and 30% higher than during non-high-O3 days ($p < 0.01$). It is unlikely that the local emissions of these air pollutants changed substantially between high-O3 and non-high-O3 days. Because more O3 precursors were usually consumed by intensive photochemical reactions on high-O3 days, the more abundant O3 precursors on high-O3 days might indicate poor dispersion and dilution of air pollutants. Conversely, higher levels of isoprene were observed during daytime than at night, suggesting that biogenic emission (BVOCs) of isoprene was more enhanced than its photochemical oxidation and dispersion during daytime hours. Isoprene is often used as a tracer of biogenic sources, as it is the most abundant compound in vegetation emissions (Guenther et al., 2006; Sharkey et al., 2008). Mixing ratios of isoprene were comparable ($p > 0.05$) on both high-O3 and non-high-O3 days, indicating that there was no significant difference in biogenic emissions between the two scenarios.

### 3.2. Source apportionment of ambient VOCs

#### 3.2.1. Source contribution to VOCs

Seven factors were identified by the PMF to best describe the sources of ambient VOCs: gasoline exhausts, diesel and compressed natural gas (CNG) exhausts, stationary combustion, the petrochemical industry, solvent usage in painting, asphalt application, and biogenic VOCs (BVOCs) (see Text S3 and Fig. S4 in the supplement for further description). Table 1 lists the source contributions to the total mixing ratios of VOCs used for source apportionment on high-O3 days and non-high-O3 days, in the forms of mixing ratio and percentage contribution. Notably, vehicle emissions, including gasoline exhaust, and diesel and CNG exhausts, were the dominant sources of VOCs, with total contributions of 45.4 ± 5.2% (11.0 ± 2.1 ppbv) and 37.3 ± 2.9% (7.1 ± 1.0 ppbv) during high-O3 and non-high-O3 days, respectively. The contribution of vehicular exhausts to VOCs in this study was comparable to that found at an urban site in Hong Kong (Ling and Guo, 2014), while lower than in Beijing (Liu et al., 2005). In addition, stationary combustion was an important contributor to ambient VOCs, with a contribution of 31.5 ± 4.5% (5.6 ± 0.6 ppbv) during high-O3 days and 36.5 ± 2.7% (4.9 ± 0.3 ppbv) during non-high-O3 days. This finding is not unreasonable, in view of the considerable coal consumption in Wuhan (more than 17 million tons in 2015) and intensive burning of biomass (e.g. crop residues) in and around Wuhan (Lyu et al., 2016).

In comparison, VOCs emitted from diesel and CNG exhausts and solvent usage in painting on high-O3 days were much higher than during non-high-O3 days ($p < 0.01$). However, gasoline exhaust, asphalt application, stationary combustion, and BVOCs made comparable contributions to VOCs between high-O3 and non-high-O3 days ($p > 0.05$). In addition, VOCs attributable to the petrochemical industry were even lower during high-O3 days ($p < 0.01$). However, because the reactivity of VOC species in O3 formation varies over a wide range (Carter, 1994), we could not conclude that the sources with higher contributions to VOCs (vehicle exhausts, stationary combustion, and solvent usage) were responsible for the occurrence of high-O3 days. In other words, further investigation was needed into the contributions of VOC sources to O3 production.

![Fig. 2. Average diurnal patterns of grouped VOCs on high-O3 days (78 samples) and non-high-O3 days (487 samples).](image)
reactivity participate more in photochemical reactions during high-
were included for source apportionment. Because species with high
study for daytime hours (07:00–19:00 LST). In fact, O3 simulation
to construct the base scenario, while in the constrained scenario
high-O3 days discussed in section 3.1 (August 17) was involved. This
source were deducted. Two scenarios for O3 simulation (a base scenario and a con-
level and diurnal trends of O3, implying that O3 on these days was mainly locally formed. However, O3 was only simulated in this study for daytime hours (07:00–19:00 LST). In fact, O3 simulation by a chemical transport model in the same period indicated that while local formation was responsible for daytime O3, regional transport elevated nocturnal O3 (more details are given in 3.3).

Table 2 summarizes the contributions of VOC sources to O3 production on high-O3 days and non-high-O3 days. It was found that vehicle exhausts (exhausts from gasoline-, diesel- and CNG-fueled vehicles) made the largest contribution to O3 production, with 34.0 ± 1.4% (13.9 ± 2.2 ppbv) during high-O3 days and 29.5 ± 0.7% (8.3 ± 0.9 ppbv) during non-high-O3 days. However, compared to their contributions to VOCs (45.4 ± 5.2% during high-
O3 days, and 37.3 ± 2.9% during non-high-O3 days; \( p < 0.01 \)) the contribution of vehicle exhausts to O3 production was lower (\( p < 0.01 \)). In contrast, the contributions to O3 production of the petrochemical industry, solvent usage in painting, and BVOCs were obviously higher than their contributions to VOCs (\( p < 0.01 \)). This discrepancy might be caused by the source-specific compositions of VOCs and the different reactivity of VOCs in O3 formation. More importantly, we noticed that O3 produced by vehicle exhausts (the sum of exhausts from gasoline-, diesel- and CNG-fueled vehicles) and stationary combustion all increased significantly during high-O3 days (\( p < 0.05 \)). In particular, O3 produced by VOCs from diesel and CNG exhausts increased from 13.7 ± 0.6% (3.9 ± 0.4 ppbv) during non-high-O3 days to 19.2 ± 1.3% (7.8 ± 1.3 ppbv) during high-O3 days. This finding implies that emission of VOCs from diesel and CNG exhausts was the main culprit for elevated O3 on high-O3 days.

### 3.2.2. Source contributions to \( O_3 \) production

To further understand the contributions of different VOC sources to \( O_3 \) formation, the in situ production of \( O_3 \) was simulated using the PBM-MCM model. Because photolysis rates could not be well calibrated on rainy days and wet deposition was not considered in the model, there were often major discrepancies between observed and simulated \( O_3 \) on rainy days. Therefore, days with precipitation (in total 10 days) were excluded in the \( O_3 \) simulation. In addition, the instruments were maintained on some days to guarantee data quality. These days were also omitted from the \( O_3 \) simulation.

Fig. 5 in the supplement shows the model validation results. These indicate that the PBM-MCM model well reproduced the levels and diurnal trends of \( O_3 \), implying that \( O_3 \) on these days was mainly locally formed. However, \( O_3 \) was only simulated in this study for daytime hours (07:00–19:00 LST). In fact, \( O_3 \) simulation by a chemical transport model in the same period indicated that while local formation was responsible for daytime \( O_3 \), regional transport elevated nocturnal \( O_3 \) (more details are given in 3.3).

Table 2 summarizes the contributions of VOC sources to \( O_3 \) production on high-O3 days and non-high-O3 days. It was found that vehicle exhausts (exhausts from gasoline-, diesel- and CNG-fueled vehicles) made the largest contribution to \( O_3 \) production, with 34.0 ± 1.4% (13.9 ± 2.2 ppbv) during high-O3 days and 29.5 ± 0.7% (8.3 ± 0.9 ppbv) during non-high-O3 days. However, compared to their contributions to VOCs (45.4 ± 5.2% during high-
O3 days, and 37.3 ± 2.9% during non-high-O3 days; \( p < 0.01 \)) the contribution of vehicle exhausts to \( O_3 \) production was lower (\( p < 0.01 \)). In contrast, the contributions to \( O_3 \) production of the petrochemical industry, solvent usage in painting, and BVOCs were obviously higher than their contributions to VOCs (\( p < 0.01 \)). This discrepancy might be caused by the source-specific compositions of VOCs and the different reactivity of VOCs in \( O_3 \) formation. More importantly, we noticed that \( O_3 \) produced by vehicle exhausts (the sum of exhausts from gasoline-, diesel- and CNG-fueled vehicles) and stationary combustion all increased significantly during high-O3 days (\( p < 0.05 \)). In particular, \( O_3 \) produced by VOCs from diesel and CNG exhausts increased from 13.7 ± 0.6% (3.9 ± 0.4 ppbv) during non-high-O3 days to 19.2 ± 1.3% (7.8 ± 1.3 ppbv) during high-O3 days. This finding implies that emission of VOCs from diesel and CNG exhausts was the main culprit for elevated \( O_3 \) on high-O3 days.

### 3.3. Contributions of local formation and regional transport to \( O_3 \) levels

To understand the causes of high-\( O_3 \) days in Wuhan during the sampling period, the local formation and regional transport of \( O_3 \) during the continuous sunny days from August 13 to 18 were simulated as a case study using the WRF-CMAQ model. One of the high-\( O_3 \) days discussed in section 3.1 (August 17) was involved. This case was selected to represent the general characteristics of high-\( O_3 \) days during the sampling period, as all the high-\( O_3 \) days occurred under similar meteorological conditions (see section 3.1). The processes influencing \( O_3 \) concentration, i.e. advection and diffusion in the horizontal and vertical directions, dry deposition, and chemical reactions, were fully considered in the WRF-CMAQ model. The model configurations were consistent with those described in Jiang et al. (2010). Fig. 3 shows the hourly variations of the simulated and observed \( O_3 \) through August 13 to 18, 2016, in Wuhan. The model well reproduced the observed \( O_3 \) in both magnitude and diurnal pattern, with an index of agreement of 0.79 (Willmott, 1981).

It is noteworthy that the WRF-CMAQ overestimated \( O_3 \) on August 15–16, but underestimated \( O_3 \) on August 13, 17, and 18.

### Table 1

Source contributions to VOCs on high-\( O_3 \) days and non-high-\( O_3 \) days (mean ± 95% confidence interval).

<table>
<thead>
<tr>
<th>Source</th>
<th>Mixing ratios (ppbv)</th>
<th>Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High-( O_3 ) days</td>
<td>Non-high-( O_3 ) days</td>
</tr>
<tr>
<td>Gasoline exhaust</td>
<td>4.7 ± 0.9</td>
<td>3.7 ± 0.5</td>
</tr>
<tr>
<td>Diesel and CNG exhausts</td>
<td>6.3 ± 1.6</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>(Vehicle exhausts)</td>
<td>(11.0 ± 2.1)</td>
<td>(7.1 ± 1.0)</td>
</tr>
<tr>
<td>BVOCs</td>
<td>0.5 ± 0.1</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>Stationary combustion</td>
<td>5.8 ± 0.6</td>
<td>4.9 ± 0.3</td>
</tr>
<tr>
<td>Asphalt application</td>
<td>1.5 ± 0.6</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>Solvent usage in painting</td>
<td>1.5 ± 0.3</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Petrochemical industry</td>
<td>0.9 ± 0.2</td>
<td>1.1 ± 0.1</td>
</tr>
</tbody>
</table>

### Table 2

Source contributions to \( O_3 \) production on high-\( O_3 \) days and non-high-\( O_3 \) days (mean ± 95% confidence interval).

<table>
<thead>
<tr>
<th>Source</th>
<th>Net ( O_3 ) increment (ppbv)</th>
<th>Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High-( O_3 ) days</td>
<td>Non-high-( O_3 ) days</td>
</tr>
<tr>
<td>Gasoline exhaust</td>
<td>6.1 ± 0.9</td>
<td>4.5 ± 0.4</td>
</tr>
<tr>
<td>Diesel and CNG exhausts</td>
<td>7.8 ± 1.3</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td>(Vehicle exhausts)</td>
<td>(13.8 ± 2.2)</td>
<td>(8.3 ± 0.8)</td>
</tr>
<tr>
<td>BVOCs</td>
<td>6.9 ± 1.1</td>
<td>6.0 ± 0.8</td>
</tr>
<tr>
<td>Stationary combustion</td>
<td>5.3 ± 0.7</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td>Asphalt application</td>
<td>3.3 ± 0.5</td>
<td>2.7 ± 0.4</td>
</tr>
<tr>
<td>Solvent usage in painting</td>
<td>5.9 ± 0.9</td>
<td>4.8 ± 0.5</td>
</tr>
<tr>
<td>Petrochemical industry</td>
<td>4.9 ± 0.7</td>
<td>3.8 ± 0.4</td>
</tr>
</tbody>
</table>
The PBM-MCM model overestimated O$_3$ on August 17, 19, 24, and 31 (Fig. S5). Despite the discrepancies, the modeling results were acceptable, in view of the uncertainties inherent in model simulations. For the WRF-CMAQ model, the uncertainty mainly derives from the uncertainty of the emission inventory and the carbon bond chemical mechanisms. Though the PBM-MCM model is near-explicit in chemical mechanisms, it does not consider the physical processes. Therefore, some differences can be expected between the observed O$_3$ and simulated O$_3$ for both models. In fact, this discrepancy is common in almost all studies that use these chemical transport models and box models (e.g., Gao et al., 2016; Wang et al., 2017; Chen et al., 2018).

The contributions of different processes to O$_3$ are summarized in Table 3. Overall, horizontal advection ($-1.3 \pm 7.0$ ppbv) and diffusion ($-0.1 \pm 0.02$ ppbv) made negative contributions to O$_3$ mixing ratios. In addition, $3.4 \pm 0.6$ ppbv of O$_3$ was removed through dry deposition. In contrast, O$_3$ was elevated by $3.9 \pm 7.5$ and $14.2 \pm 1.2$ ppbv due to vertical advection and diffusion, respectively. As the largest contributor to O$_3$, chemical reactions built up the O$_3$ mixing ratio by $42.3 \pm 6.1$ ppbv. It is noteworthy that the chemical reactions indicated the process of local O$_3$ formation. Because advection and diffusion generally represent the transport of air pollutants, the sum of horizontal and vertical advection/diffusion is referred to hereafter as regional transport (Jiang et al., 2010; Li et al., 2012; Chen et al., 2018). Regional transport, local photochemical formation, and dry deposition accounted for $44.4 \pm 5.8\%$, $60.2 \pm 6.1\%$ and $-4.6 \pm 0.5\%$ of the total simulated O$_3$, respectively. More specifically, the contribution of regional transport ($59.1 \pm 9.9\%$) to nighttime O$_3$ predominated over local formation ($42.7 \pm 10.1\%$) (20:00–06:00 LST), while daytime O$_3$ was mainly derived from local photochemical formation ($74.7 \pm 5.8\%$), about twice the regional transport ($32.2 \pm 5.4\%$). Therefore, it would seem that the high daytime O$_3$ on high-O$_3$ days in Wuhan is primarily attributable to local formation, while regional transport from the east made significant contributions to nocturnal O$_3$. In fact, compared to the same time slots on other days, the observed nighttime O$_3$ increased by 4–12 ppbv on August 15–17 (Fig. 3), in contrast to limited nocturnal O$_3$ production from photochemical reactions and the consumption of O$_3$ by some substances (e.g., NO and alkenes). As such, the increase of nocturnal O$_3$ on these days is most likely attributable to regional transport, consistent with the modeling results.

### 3.4 Implications for control strategies

To understand O$_3$ formation mechanisms, the relationships between O$_3$ and its precursors were explored using the PBM-MCM model. O$_3$ precursors were divided into four groups, namely anthropogenic volatile organic compounds (AVOCs), BVOCs, CO, and NO$_x$; their RIR values were calculated using Eq. (3). According to previous studies (Zhang et al., 2006; Lyu et al., 2016b; Wang et al., 2018), the positive RIR value of VOCs and negative RIR value of NO$_x$ indicate VOCs-limited O$_3$ production in the study area, while the negative RIR value of VOCs and positive RIR value of NO$_x$ mean that production is NO$_x$-limited. Fig. S6 shows the mean RIR values of O$_3$ precursors over the high-O$_3$ and non-high-O$_3$ days. It indicates that the average RIR values of VOCs (AVOCs and BVOCs) were positive, while RIR for NO$_x$ was negative, indicating that O$_3$ formation was limited by VOCs at this site on both high-O$_3$ days and non-high-O$_3$ days.

**Table 3**

Factor contributions to the simulated O$_3$ during August 13–18, 2016, in Wuhan (Unit: ppbv).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Average ± 95% Confidence Interval</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal advection</td>
<td>$-1.3 \pm 7.0$</td>
<td>125.0</td>
<td>-111.5</td>
<td>42.7</td>
</tr>
<tr>
<td>Vertical advection</td>
<td>$3.9 \pm 7.5$</td>
<td>127.8</td>
<td>-128.3</td>
<td>45.5</td>
</tr>
<tr>
<td>Horizontal diffusion</td>
<td>$-0.1 \pm 0.02$</td>
<td>0.1</td>
<td>-0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Vertical diffusion</td>
<td>$14.2 \pm 1.2$</td>
<td>36.6</td>
<td>1.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>$-3.4 \pm 0.6$</td>
<td>-0.01</td>
<td>-10.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Chemical reactions</td>
<td>$42.3 \pm 6.1$</td>
<td>130.5</td>
<td>-8.0</td>
<td>36.9</td>
</tr>
</tbody>
</table>

Fig. 3. Time series of simulated and observed O$_3$ concentrations in Wuhan from 00:00 LST, August 13 to 23:00 LST, August 18, 2016. The grey area defines the lowest and highest simulated O$_3$ at eight air quality monitoring stations (AQMSs) surrounding the sampling site. The AQMSs are managed by the China National Environmental Monitoring Centre.
production, while reducing NOx would lead to O3 increase. A VOC-limited regime was also identified in rural areas of Delhi, India (Kumar et al., 2017), and in urban and suburban Hong Kong (Lyu et al., 2016b). However, Lin et al. (2017) indicated that summertime O3 pollution in the southeastern U.S. was alleviated by controlling NOx emissions, indicating a NOx-limited regime in O3 formation. Jin et al. (2017) also found that O3 production became increasingly sensitive to NOx in mid-latitude megacities in the northern hemisphere (e.g., New York, London, and Seoul) between 2005 and 2015. It should be noted that a recent study (McDonald et al., 2018) pointed out the underestimation of VOC emissions from volatile chemical products in industrialized cities in the U.S., meaning that the current understandings of O3 formation mechanisms based on pre-existing emission inventories might need further verification. To sum up, O3-VOC-NOx sensitivity should be investigated case by case. This study expands the worldwide database of O3-VOC-NOx sensitivity to include the situation in developing regions, where NOx is at high levels and might continue to increase if no stringent control strategies are put in place (Jin et al., 2017).

Further, the RIR of AVOCs was much higher than that of BVOCs. Thus, O3 formation was more sensitive to AVOCs, which should be focused on in O3 abatement. In addition, relatively high average RIR was found for CO (RIR = 0.40), indicating that CO had a positive impact on O3 formation in Wuhan, in contrast to the findings of Wang et al. (2017), who reported that the RIR value of BVOCs was much higher than CO in summer in Hong Kong.

To further investigate the role of NOx in O3 chemistry, O3 productions with different levels of NOx were simulated using the PBM-MCM model. Table S5 shows the mean net O3 production in the base case with the observed NOx and in the constrained cases with NOx reduced by 10%, 20%, 40%, 60%, 80%, 90%, 95%, and 98%. The observed VOCs were applied to all the cases without any reduction. It was found that as NOx reduction percentages increased from 10% to 95%, the simulated O3 also increased, by a percentage rising from 2% to 78%. The implication is that O3 formation is limited by VOCs in these cases. However, simulated O3 decreased significantly when the reduction percentage of NOx increased from 95% to 98%, indicating that O3 formation switched to the NOx-limited regime. The dual role of NOx in O3 formation is clearly presented in these experiments.

Because VOCs (particularly AVOCs) and NOx are generally co-emitted, it is nearly impossible to only reduce VOC emissions while NOx remains unchanged. Therefore, it is vital to find an appropriate reduction ratio of VOCs/NOx for effectively controlling O3 pollution. With the aid of the PBM-MCM model, the net O3 variations were simulated in the scenarios with different percentage cuts in VOCs and NOx, based on the measured VOCs and NOx. The positive and negative variations indicated increases and decreases of O3, respectively. The percentage cuts in VOCs and NOx were 0%–50%, at 10% intervals. As shown in Fig. S7, the net O3 variation increased non-linearly with the increase of percentage cuts in NOx and decreased with the increase of percentage cuts in VOCs. This finding is consistent with the finding that O3 formation occurred in a VOC-limited regime during the study period in Wuhan. For reducing O3 production, the percentage cuts in VOCs and NOx were only considered acceptable when O3 variations were nil or negative. According to Fig. S7, with the increase of percentage cuts in VOCs from 10.0% to 50.0%, the maximum percentage cut in NOx for nil O3 increment increased from 13.7% to 51.0%, and the ratio of the VOCs percentage cut to NOx percentage cut (termed the "VOCs/NOx cutting ratio") increased from 0.73 to 0.98. Therefore, to maintain a nil/negative O3 increment, the VOCs/NOx cutting ratio should be higher than 0.73, given that VOCs were cut by 10%–50%. This finding could guide the formulation and implementation of effective O3 control strategies in Wuhan.

4. Conclusions

In this study, continuously measured data of speciated VOCs, trace gases, and meteorological parameters in August 2016 at an urban site in Wuhan were analyzed to explore the different characteritics of VOCs and O3 pollution between high-O3 and non-high-O3 days. Results indicated that high temperature, low wind speed, low relative humidity, tropical cyclones, and transport of polluted air masses from northern China to Wuhan were favorable for the occurrence of high-O3 days during the study period. During high-O3 days, the mixing ratios of O3, CO, and TVOCs were 61.2 ± 7.4, 987.8 ± 95.4 and 43.9 ± 3.8 ppbv, about 40%, 37%, and 33% higher than during non-high-O3 days (p < 0.01, respectively. However, the levels of NO (ΔNO: −1 ppbv) and NO2 (ΔNO2: −2 ppbv) were comparable between high-O3 and non-high-O3 days (p > 0.05).

Seven VOC sources were identified: gasoline exhaust, diesel and CNG exhausts, stationary combustion, petrochemical industry, solvent usage in painting, asphalt application, and BVOCs. Vehicle exhausts (i.e., gasoline exhaust, diesel and CNG exhausts) made the largest contribution to VOCs and O3 production during both high-O3 days (45.4 ± 5.2%) and non-high-O3 days (37.3 ± 2.9%). The contributions of vehicle exhausts and stationary combustion to VOCs and O3 production increased remarkably from non-high-O3 days to high-O3 days, suggesting that these sources were the culprit for elevated O3 during high-O3 days. Ozone simulation using the WRF-CMAQ model indicated that while local formation (74.7 ± 5.8%) accounted for most of the daytime O3, the nighttime O3 was significantly elevated by regional transport (59.1 ± 9.9%). As indicated by the relationship between O3 and its precursors, O3 formation in urban Wuhan was VOC-limited, and the sensitivity of O3 formation to AVOCs predominated over BVOCs and CO. To effectively control O3 pollution, the reduction ratio between VOCs and NOx should be higher than 0.73. In addition, because VOCs emitted from vehicle exhausts were the main contributors to O3 production, it is urgent and effective to control vehicle emissions to pursue O3 reduction in Wuhan. This study fills the knowledge gap concerning the causes of high O3 events in Central China, particularly the characterization of local and regional contributions to high O3, which will be of help for O3 study and control in other subtropical regions with moist monsoon climates.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.05.042.

References


