Characteristics of ozone pollution and the sensitivity to precursors during early summer in central plain, China

Yasong Li¹, Shasha Yin¹,*, Shijie Yu¹, Ling Bai¹, Xudong Wang¹, Xuan Lu¹, Shuangliang Ma²

¹ Research Institute of Environmental Science College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450001, China
² Henan Environmental Monitoring Center, Zhengzhou, 450004, China

A R T I C L E   I N F O
Article history:
Received 5 December 2019
Revised 8 June 2020
Accepted 16 June 2020
Available online 28 July 2020

Keywords:
H₂O₂
Meteorological influences
Ozone formation potential
Smog production model
O₃-VOC-NOₓ

A B S T R A C T
In this study, we conducted an observation experiment from May 1 to June 30, 2018 in Zhengzhou, a major city in central China, where ground ozone (O₃) pollution has become serious in recent years. The concentrations of O₃ and its precursors, as well as H₂O₂ and meteorological data were obtained from the urban site (Yanchang, YC), suburban (Zhengzhou University, ZZU) and background sites (Ganglishuiku, GLSK). Result showed that the rates of O₃ concentration exceeded Chinese National Air Quality Standard Grade II (93.3 ppbv) were 59.0%, 52.5%, and 55.7% at the above three sites with good consistency, respectively, indicating that O₃ pollution is a regional problem in Zhengzhou. The daily peak O₃ appeared at 15:00–16:00, which was opposite to VOCs, NOₓ, and CO and consistent with H₂O₂. The exhaustive statistical analysis of meteorological factors and chemical effects on O₃ formation at YC was advanced. The high concentration of precursors, high temperature, low relative humidity, and moderately high wind speed together with the wind direction dominated by south and southeast wind contribute to urban O₃ episodes in Zhengzhou. O₃ formation analysis showed that reactive alkenes such as isoprene and cis-2-butene contributed most to O₃ formation. The VOCs/NOₓ ratio and smog production model were used to determine O₃-VOC-NOₓ sensitivity. The O₃ formation in Zhengzhou during early summer was mainly under VOC-limited and transition regions alternately, which implies that the simultaneous emission reduction of alkenes and NOₓ is effective in reducing O₃ pollution in Zhengzhou.

© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction
Ozone (O₃) in the troposphere is an important component of photochemical smog. O₃ was first discovered in Los Angeles in 1943 and could damage the human skin, eyes, and respiratory system as well as animals and plants (Hidy, 2000; Kleinman et al., 2000). It is a secondary pollutant formed by photochemical reactions involving natural or man-made emissions of NOₓ and VOCs (Seinfeld and Pandis, 1998) under the action of solar ultraviolet radiation. Owing to the complex chemical mechanism and regional differences in emission distribution and meteorology, the relationship between O₃ and its precursors (NOₓ and VOCs) presents highly non-linear interactions.

* Corresponding author.
E-mail: shashayin@zzu.edu.cn (S. Yin).
In the past 10 years, most parts of China have been facing serious PM\textsubscript{2.5} pollution problems, especially in autumn and winter. In comparison with the gradual improvement of particle pollution during the last three years, the problem of O\textsubscript{3} pollution has become more serious (Li et al., 2017a; Liu and Wang, 2014; Liu et al., 2012), especially in the North China Plain (NCP) during summer, Yangtze River Delta (YRD), and Pearl River Delta (PRD) regions with the most populous and industrialized urban agglomeration (Li et al., 2014; Li et al., 2012; Ran et al., 2011; Tang et al., 2012). O\textsubscript{3} pollution in major urban agglomerations in China may occur at the beginning of NO\textsubscript{x} control considering the substantial reduction of NO\textsubscript{x} to lessen particulate pollution (Jiang et al., 2018a). A study in North China found that even though NO\textsubscript{x} emissions have decreased since 2012, the O\textsubscript{3} level increased by approximately 2 ppbv/year from 2003 to 2015 (Sun et al., 2016). To control O\textsubscript{3} pollution, scholars have investigated its underlying mechanism in many regions in China to explore the sensitivity of local O\textsubscript{3} formation (An et al., 2015; Cheng et al., 2010; Geng et al., 2008; Ou et al., 2016; Pan et al., 2015; Shao et al., 2009; Xue et al., 2014a; Zhang et al., 2014). Results showed that the VOCs/NO\textsubscript{x} ratio in urban areas is low, and most of them are controlled by VOCs. Active aromatics and alkenes contribute most to O\textsubscript{3} formation. Above phenomena have been observed in Guangzhou (Lu et al., 2010b; Shao et al., 2009; Zhang et al., 2008), Hong Kong (Xue et al., 2014b), Beijing (Lu et al., 2010a) and Shanghai (Geng et al., 2007). In rural areas such as Taishan (Kanaya et al., 2009), Wuqing (Ran et al., 2012) and Yanshan (Wei et al., 2015), O\textsubscript{3} formation is mostly controlled by NO\textsubscript{x} because of the high VOC emission from biological sources.

O\textsubscript{3} pollution in the central region of China, especially in Henan Province has also become severe in these years. Zhengzhou, as the capital of Henan Province, is one of the most important developing cities in Central China. This city has dense industries and population with more than 10 million residents in 2018, and more than three million vehicle population ownership in 2018, leading to increased atmospheric pollutant emissions and poor air quality (the average concentration of PM\textsubscript{2.5} in 2018 is 68.3 \text{\mu g/m}^3). At present, O\textsubscript{3} in summer has gradually replaced PM\textsubscript{2.5} as the primary air pollutant in the region. However, the characteristics of O\textsubscript{3} formation and its relationship to precursors and meteorological factors in this region remain unclear. Early studies focused on the characteristics of particulate matter and its formation mechanism (Jiang et al., 2018b).

Yu et al. (2017) preliminarily identified the states of air pollution in Zhengzhou in 2015, and reported that O\textsubscript{3} pollution was serious in June. Therefore, for the first time, we selected the typical period for exploring O\textsubscript{3} formation characteristic in early summer, taken Zhengzhou as example, to (1) identify the temporal variations of O\textsubscript{3} and its precursors, (2) analyze the meteorological and chemical effects on O\textsubscript{3} formation at urban areas, (3) discuss the distinctions between O\textsubscript{3} episode and non-episode periods, (4) assess the sensitivity of O\textsubscript{3} formation to its precursors.

1. Materials and methods

1.1. Monitoring site and period

The observation experiment was carried out from May 1 to June 30 of 2018. Three observation sites were selected including the upwind urban station Yanchang (YC), the traffic and suburban integrated site Zhengzhou University (ZZU), and the downwind suburbs background station Ganglishiku (GLSK) (Fig. 1). The YC site is mostly surrounded by residential and administrative areas and a shopping district without a major industrial source. The ZZU site is located in the university campus of the western suburbs of Zhengzhou. This site is settled at the top of the sixth floor and detailed information was described in our previous study (Wang et al., 2018). GLSK is located 20 km northeast of ZZU at the scenic area, and no major anthropogenic source can be found around it. YC and GLSK, as the national air quality monitoring stations, can reflect the O\textsubscript{3} pollution of the downtown and suburban areas, respectively.

1.2. Data source and instrument

The measurement parameters of the above sites are listed in Table S1. The concentration data of trace gases (O\textsubscript{3}, NO\textsubscript{x}, NO, and CO) of YC, GLSK, and ZZU were obtained from Zhengzhou Environmental Protection Monitoring Center Station. A series of on-line analyzers (TE, 49i, 42i and 48i) was used to obtain the concentrations of O\textsubscript{3}, NO\textsubscript{x}
(NO+NO2), and CO with a resolution of 1 h. The trace gasses are expressed in ppbv, the conversion method for μg/m3 and ppbv (Li et al., 2013) is as follows:

\[ C_V = C_M \times \frac{22.4 \times (273.15 + T)}{273.15} \times \frac{1013.25}{P} \]  

(1)

where, \( C_V \) is the volume fraction of gas, \( C_M \) is the mass concentration of gas, \( T \) and \( P \) represent temperature and pressure respectively. On-line ambient VOCs (56 NMHCs) and meteorological (Temperature, relative humidity, pressure, precipitation and wind parameters) data of YC were derived from the Henan Provincial Environmental Monitoring Center. Ambient VOCs, including 29 alkanes, 10 alkenes, 16 aromatics and 1 alkyne (ethyne) were measured using an online GC-FID (GC 5000) produced by the German AMA Company. Data were recorded at a high time resolution of 1 h. This instrumentation has been described in detail elsewhere (An et al., 2014). The DIM200 calibration module (diluted 100 times) was used for calibration for 3 weeks to ensure the validity and reliability of the observation data. The calibration gas during the observation period used mixed calibration gas supplied by the Linde Gas North America LLC. The instrument was periodically calibrated for single point calibration and peak window drift. During the calibration, the correlation coefficient was between 0.993 and 0.999. Meteorological data were obtained by an automatic weather station model QXZ 1.0 (Yigu Technologies, China).

On-line trace gas monitoring instrument (AL2021) was used to continuously monitor the concentration of H2O2 with a time resolution of 90 s at ZZU. AL2021 is an automatic continuous H2O2 analyzer from Germany AERO LASER company based on the peroxidase reaction for gas and liquid samples. In this study, an average concentration of 1 h was used, and calibration was performed every 1–3 days. Detailed information can be found in the study of Ye et al. (2018). The measured trace gas compounds and measurement principles were summarized (Table S2). The specific VOCs species were listed in Table S3. Sunrise and sunset time occurred at 06:00 and 20:00 Chinese National Standard Time, respectively.

1.3 Ozone formation analysis

VOC reactivity refers to the potential of an organic substance to form \( O_3 \) through a reaction (Carter, 1994; Chameides et al., 1992). VOC reactivity can be assessed by three main methods: calculating the propene-equivalent concentration (prop-equiv), calculating the OH consumption rate, and analyzing the \( O_3 \) formation potential (OPF) by combining the maximum incremental reactivity (MIR). In this study, we selected prop-equiv concentrations and OPF, which have good correlation and complementarity (Geng et al., 2008), to estimate atmospheric reactivity and \( O_3 \) formation contribution of each VOC species.

The principle of prop-equiv concentrations involves the comparison of all VOCs at an equal base point, considering the concentration of the species and reaction constant with OH radicals. This method has been widely used in previous studies (Duan et al., 2008; Li et al., 2017b; Ran et al., 2011; Tang et al., 2007). The prop-equiv concentration was estimated using the following equation:

\[ C_{\text{PEC}} = \frac{K_{OH}(j) \times C_{VOC}}{K_{OH}(C_3H_8)} \]  

(2)

where, \( C_{\text{PEC}} \) is the prop-equiv concentration, \( C_{VOC} \) is the actual observed VOC species atmospheric concentration expressed in ppbC, and \( K_{OH}(j) \) is the reaction rate constant of various VOC species with OH. The cumulative prop-equiv concentration represents the sum of the individual prop-equiv concentrations. \( K_{OH}(C_3H_8) \) expresses the chemical reaction rate constant of propene with OH.

The reactivity of single VOC species is different, and the reaction partner in the mixture of VOCs undergoes competition, resulting in changes in the reaction pathway and \( O_3 \) formation yield. OPF is a widespread method for estimating the maximum \( O_3 \) production of individual VOC species from which the dominant \( O_3 \) forming species can be identified (Xu et al., 2015). OPF can be expressed as follows:

\[ \text{OPF} = C_j \times \text{MIR}_j \]  

(3)

where, \( \text{OPF} \), is the \( O_3 \) formation potential of VOC species \( j \), \( C_j \) is the atmospheric concentration of VOC species \( j \) expressed in ppbv, and \( \text{MIR}_j \) is the \( O_3 \) formation coefficient of VOC species \( j \) in the maximum incremental reaction of \( O_3 \).

The \( K_{OH} \) and MIR values of VOC species were derived from the studies of Atkinson (1986) and Carter (2010), respectively. Although the \( K_{OH} \) values of n-dodecane is lacking, the actual volume fraction of it in YC site is very low, which was omitted in this study.

1.4 Smog production algorithm

The smog production model (SPM) is an observation-based model that uses a series of semi-empirical formulas to calculate the extent of photochemical reaction (\( E \)); this model was initially developed by Graham Johnson and his research team (Johnson, 1984). They called the integrated empirical rate (IER) model. Then, Blanchard et al. (1999) modified the IER and reformulated the smog production algorithm by using smoke chamber data and model simulation results to improve the accuracy of \( O_3 \) sensitivity prediction. The model was used to study the sensitivity of \( O_3 \) formation to changes in NOx and VOCs concentrations in the current state (Li et al., 2014; Li et al., 2017b; Tang et al., 2012).

The extent of reaction \( E(t) \) is defined as follows:

\[ E(t) = \frac{\text{SP}(t)}{\text{SP}_{\text{max}}} = \frac{O_3(t) + DO_3(t) - 0_3(0) + NO(i) - NO(t)}{\beta[NO_x(t)]} \]  

(4)

where, \( \text{SP} \) represents the total amount of NO consumed and \( O_3 \) produced which is also known as the photochemical smog yield, \( \text{SP}_{\text{max}} \) represents the photochemical smog yield at time \( t \), \( \text{SP}_{\text{max}} \) represents the maximum photochemical smog yield from the initial time to time \( t \), \( O_3(t) \) is the \( O_3 \) concentration at time \( t \), \( DO_3(t) \) represents the cumulative deposition loss at time \( t \). The specific calculation method of \( DO_3 \) can be found in literature (Blanchard et al., 1999). In this study, the value of \( DO_3(t) \) from 06:00–18:00 was calculated by setting 06:00 as the initial time. \( O_3(t) \) represents the background concentration of ambient \( O_3 \), \( NO(i) \) and \( NO_x(t) \) represent the mass of NO and \( NO_x \) input to the system from the initial time to time \( t \), respectively, and \( NO(t) \) is the NO concentration at time \( t \). \( \alpha \) and \( \beta \) are empirical parameters. \( NO_x(t) \) and \( NO(t) \) were calculated using Eqs. (5)–(6), where \( NO_x(t) \) represents the \( NO_x \) concentration at time \( t \) and \( F \) is the empirical parameter. In the formula,
Fig. 2 – Time series of the average hourly concentration for (a) O₃, (b) NO₂, (c) O₂, (d) NO, (e) CO, (f) H₂O₂ and (g) VOCs at ZZU (black), YC (red) and GLSK (blue) station. The horizontal line (red) in panel (a) denotes the hourly average Chinese national ambient air quality standard II for O₃ of 93.3 ppbv. Vertical dotted lines indicate the 0 h for each day.

X was determined using Eqs. (7)–(9).

\[ \text{NOx}(t) = \text{NOx}(t) + \left( \frac{\beta}{3F} \right) (2X + 1)^3 \]  

\[ \text{NO}(t) = F \times \text{NOx}(t) \]  

\[ X = \cos \left[ \frac{4r + \cos^{-1}(C)}{3} \right] \]  

\[ C = 1 - \frac{27(\gamma/F)}{(2(\mu/F))^2} \]  

\[ \gamma = O₃(t) + DNO₂(t) - O₃(0) + F \times \text{NOx}(t) - \text{NO}(t) \]  

In Eqs. (4)–(6), all species are expressed in ppbv. The values of empirical parameter in the formula are shown in Table S4 (Blanchard et al. 1999). Based on the above formula, the photochemical reaction extent E(t) was calculated. For the SPM results, the reaction extent E(t) < 0.6 represents a system under VOC control, E(t) > 0.9 represents a system under NOx control, and 0.6 < E(t) < 0.9 represents the transition control region (Blanchard and Stoeckenius, 2001).

2. Results and discussion

2.1. General description of air pollutant

The time series of hourly average concentrations of O₃, NO, NO₂, O₂, CO, H₂O₂ and VOCs during the period are shown in Fig. 2. In general, the O₃ concentrations show a relatively good agreement at these sites, with hourly mean concentrations of 54.8 ppbv in ZZU, 55.4 ppbv in YC, and 49.1 ppbv in GLSK. However, the corresponding values of NO₂ were 20.3, 19.4, and 15.9 ppbv at these sites. The concentrations of CO at ZZU and YC sites were close but were lower than those at GLSK in the suburban region. The H₂O₂ concentration in ZZU ranged from 0.03 ppbv to 6.06 ppbv, with an average of 2.17 ppbv. The total VOCs concentrations in YC ranged from 12.55 ppbv to 195.32 ppbv with an average of 47.2 ppbv.

The O₃ exceedance day is defined as the instance when the daily maximum average hourly O₃ concentration exceeds the Chinese National Air Quality Standard Grade II (93.3 ppbv). During the whole period (WP), the proportions of O₃ exceedance day in ZZU, YC, and GLSK were 52.5%, 59.0%, and 55.7%, respectively. The proportions in May were lower than those in June with the highest number in GLSK (38.7%). However, in June, all proportions exceeded 70.0% with the highest value in YC (90.0%). Considering YC site as an example, three heavy O₃ pollution episodes can be identified, from 8 to 10 May (EP1), 31 May to 8 June (EP2), and 19 June to 23 June (EP3). This finding indicated that O₃ pollution was serious in the early summer in Zhengzhou, and June was the suitable time to conduct our research.

Furthermore, the mean diurnal profiles of O₃, O₂ (O₃+NO₂), NO₃, NO₂, NO, CO, VOCs, and H₂O₂ concentrations are depicted (Fig. 3). In general, the diurnal variations of O₃ at ZZU, YC, and GLSK were similar, and the peak value appeared at 15:00–16:00. Subsequently, O₃ started to decrease and reached the minimum at 06:00. During daytime, the O₃ level at GLSK in suburb was slightly higher than that at ZZU and YC in urban, but it was lower during nighttime. The above phenomena can be explained as the follows: in
the daytime, compared with the urban area, more VOCs emissions from natural sources and weaker “NO titration effect” in suburb are more conducive to the generation and accumulation of \( O_3 \); at night, the relative humidity in suburb is higher than that in urban, which is more conducive to the gas-phase reaction and heterogeneous reaction of removing \( O_3 \); in addition, suburb is relatively conducive to the diffusion of pollutants, so the concentration of \( O_3 \) in suburb at night is lower than that in urban. The precursors (CO, NO\(_x\) and VOCs) of \( O_3 \) have similar diurnal patterns. The peak value occurred during the morning rush hours, and a high value was recorded at night, and the minimum value was recorded in the afternoon, which may be due to the diurnal cycle of planetary boundary layer, the local emission characteristics, and UV radiation. Similar results were observed in other cities (Li et al., 2017b; Xu et al., 2011). In comparison with \( O_3 \) and considering YC as an example, NO\(_x\) and VOCs demonstrated opposite patterns, and a valley value was recorded at 15:00 under which the photochemical reaction was strong. In addition, the daily average concentration of CO in GLSK was higher than that in ZZU and YC. Moreover, the NO\(_x\) concentrations of the three sites were similar, which may explain why the \( O_3 \) level in GLSK was slightly higher than that in ZZU and YC.

\( O_3 \), the sum of \( O_3 \) and NO\(_x\), is a good indicator of \( O_3 \) pollution and can also estimate the total atmospheric oxidant potential (Jenkin, 2004; Lin et al., 2008). As shown in Fig. 3b, \( O_3 \) has similar patterns compared with \( O_3 \); \( O_3 \) starts to increase after sunrise mainly due to \( O_3 \) increase. However, NO\(_2\) cannot regenerate \( O_3 \) at nighttime due to the lack of sunlight. \( O_3 \) drops after sunset may be caused by deposition. The \( O_3 \) concentrations at ZZU and YC were similar and were higher than that at GLSK during nighttime. However, from 9:00 in the morning its level at GLSK gradually approached in ZZU and YC, which indicated that urban site has higher atmospheric oxidation capacity than suburb. For \( H_2O_2 \), as shown in Fig. 3h, the maximum value was recorded at 16:00–17:00. Subsequently, \( H_2O_2 \) started to decrease and reached the minimum value at 06:00, which was similar with \( O_3 \).

2.2. Meteorological and chemical effects on ozone formation in the urban area

We considered YC as an example to study the effects of meteorological factors on \( O_3 \) formation. The overall weather conditions in YC during the observation period are shown in Fig. S1. The mean temperature (T) and relative humidity (RH) were 25.5°C and 61.2%, respectively. The peak T and RH were 36.6°C and 98.8%, which occurred on June 12 and May 20, respectively. These conditions presented a typical unimodal diurnal pattern. No substantially change in atmospheric pressure was observed, which was stable approximately 990 kPa, and precipitation did not occur during the observation period. The wind frequency rose is shown in Fig. S2. The frequency of wind direction (WD) was divided into five wind speed (WS) ranges: <1, 1–2, 2–3, 3–4 m/sec, and ≥4 m/sec. During the observation period, the wind field was dominated by S, SSE, and NNE winds with wind frequencies of 21.1%, 21.8%, and 12.0%, respectively. Strong SSE and S winds were ob-
erved, while the WS was below 4 m/s generally, implying the dominance of local air masses at the YC site.

In the following discussion, data were grouped into subsets representing the entire day (00:00–24:00), daytime (06:00–19:00), and nighttime (20:00–05:00) in summer.

2.2.1. Temperature and relative humidity
Temperature (T) directly affects the rate of chemical kinetics rates and the mechanism of O₃ formation and is thus often used as a predictor of O₃ episode events (Steiner et al., 2010; Wise, 2009). The ground-level O₃ concentration was directly positively correlated with T (Fig. S3(a) and (b)), when the T ranged from 31°C to 37°C, the O₃ level was close to or even exceeded 93.3 ppbv. Besides, the daytime O₃–T slope was steeper than that during nighttime. Notably, the observed correlation between the average concentration of O₃ and temperature is not only due to the temperature dependence of the chemical reaction rate, but also because high T is usually strongly correlated with stagnant, sunny or atmospheric conditions.

The dependence of the mean O₃ concentration on RH at day and night is shown in Fig. S3(c) and (d). As the RH increases, the average concentration of O₃ decreases with time, whether during day or night. A reasonable explanation is that high RH in early summer causes increased clouds and weak UV radiation, thus reducing the O₃ production rate, meanwhile, high temperature and high level of UV radiation are mostly accompanied with low RH in early summer, which will be beneficial to the formation of O₃.

2.2.2. Wind direction
The wind frequency diagrams of O₃ concentrations during daytime and nighttime are shown in Fig. S4. The diagram was divided into five O₃ concentration ranges according to the frequency of WD: 0–30, 31–60, 61–90, 91–120 and >120 ppbv. The main ground WD during daytime and nighttime were SSE, S, and NNE, with wind frequencies of 19.8%, 17.2%, and 11.9% during daytime and 23.1%, 26.4%, and 9.9% during nighttime, respectively. Whether during day or night, when the wind traveled from S and SSE, a high O₃ concentration was observed. An industrial park called Jiu long Town is located 24 km from the SSE direction of YC site and has many logistics parks. In addition, two refueling stations are located 6 km southeast of YC and 1.5 km south of YC. Therefore, the SSE and southern regions of YC are likely caused of VOC emissions, leading to strong O₃ pollution. The Yellow River is located 30 km north of YC, and the eastern region of YC is a university park with many schools and few potential emission sources. This set-up explains why the O₃ concentration is not as high as that in the SSE direction.

2.2.3. Correlation analysis
The Pearson’s correlations of O₃ at YC with other species (NO₂, NO, NOₓ, CO, and VOCs) and the meteorological parameters were calculated using SPSS 25.0. As shown in Table 1, O₃ had a significant negative correlation with its precursors during day and night. All precursors were more correlated with O₃ during the day than at night, because O₃ was mainly formed through photochemical processes. During the whole day, NO₂, NO, NOₓ, CO, and VOCs were positively and significantly correlated with one another, indicating that they were mainly affected by some common factors and primarily diffused from sources of similar or common emission. During the whole day, the absolute correlation coefficient (R) of VOCs-NOₓ correlation was larger than that of VOCs-CO, indicating that VOC is more closely related to NOₓ than to CO.

As shown in Fig. S5 and Table 1, during the whole day, T was mainly positively correlated with O₃ and negatively correlated with O₃ precursor. Meanwhile, RH was negatively correlated with O₃ and positively correlated with NO precursor. The positive correlation between O₃ and T was mainly due to the contribution of T to the formation of photochemical O₃ (Dueñas et al., 2002), which explains the relationship between the two variables. As cloud abundance increases with increasing RH, the photochemical processes associated with O₃ production slows down, and O₃ consumption increases (Londhe et al., 2008). Thus, a negative correlation between O₃ and RH was observed, similar to previous reports (Mavroidis and Ilià, 2012; Tu et al., 2007). In addition, the R value of the T–RH correlation is −0.6683, which may also indirectly lead to the above relationship.

A weak positive correlation between O₃ and wind speed (WS) was observed (Table 1), and the absolute R value of O₃–WS correlations during daytime and nighttime were 0.3289 and 0.3654, respectively, which suggested the promoting effect of WS on local O₃ formation. As shown in Section 3.2, O₃ has a typical day and night change, maintaining the highest value throughout the day between 11:00 and 16:00. The variation of O₃ mean concentrations at 11:00–16:00 under different WS was analyzed to further evaluate the WS effect on surface O₃ (Fig. 4). As WS increased from a standstill value (<1 m/s), the mean concentrations of O₃ remarkably increased. The maximum O₃ mean concentration with the wind speed ranged from 2 m/s to 4 m/s, and then became stable. With increasing WS, the stability of the boundary layer begins to decrease, and more O₃ is transported from the upper layer to the surface layer (Lal et al., 2000). However, the increase in WS promotes atmospheric mixing, dispersion, and transport, thereby facilitating the dilution of O₃ and stabilizing or even decreasing the O₃ concentration. Similar relationships between O₃ and WS were observed in other cities such as Ningbo (Tong et al., 2017) and Hangzhou (Li et al., 2017b).

2.3. Ozone formation in urban area: episode versus non-episode

2.3.1. Meteorological parameters
To eliminate the effects of rainy days, we chose a non-episode period (May 14–24) without precipitation called N-EP at the YC site for comparison with the episode period. The average values of trace gases and meteorological parameters during these periods are listed in Table 2. The average concentration of O₃ during N-EP was 43.0 ppbv, while the O₃ concentrations were 67.9 ppbv in EP1, 69.6 ppbv in EP2, and 60.2 ppbv in EP3. In addition, the mean concentration of O₃ precursors (NOₓ, CO, and VOCs) during N-EP was lower than that during episode periods probably because of the weak emissions and increased regional transport effects between May 14 and 24, which may be one of the important reasons for the low level of O₃.

In addition, the mean diurnal profiles of air pollutants and meteorological parameters during different periods were shown in Fig. S6. High mean T and low RH were observed during the three episodes compared with the N-EP.
Table 1 – The Pearson’s correlation coefficients among O₃, its precursors and meteorological parameters at different time range of YC site*.

<table>
<thead>
<tr>
<th>Time</th>
<th>O₃</th>
<th>NO₂</th>
<th>NO</th>
<th>NOₓ</th>
<th>CO</th>
<th>VOCs</th>
<th>T</th>
<th>RH</th>
<th>WS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire day</td>
<td>O₃</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>-0.5885</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>-0.3060</td>
<td>0.5014</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>-0.5467</td>
<td>0.9141</td>
<td>0.8072</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>-0.2978</td>
<td>0.2662</td>
<td>0.1801</td>
<td>0.2690</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VOCs</td>
<td>-0.2929</td>
<td>0.5416</td>
<td>0.5293</td>
<td>0.6027</td>
<td>0.4739</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>0.6374</td>
<td>-0.1689</td>
<td>-0.0492</td>
<td>-0.1398</td>
<td>-0.2400</td>
<td>0.0724</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RH</td>
<td>-0.5983</td>
<td>0.0692</td>
<td>0.0478</td>
<td>0.0695</td>
<td>0.3594</td>
<td>0.0317</td>
<td>-0.6683</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>WS</td>
<td>0.3817</td>
<td>-0.4665</td>
<td>-0.1952</td>
<td>-0.4049</td>
<td>-0.1029</td>
<td>-0.3693</td>
<td>0.1639</td>
<td>-0.1139</td>
</tr>
<tr>
<td>Daytime (06:00–19:00)</td>
<td>O₃</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>-0.5772</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>-0.3556</td>
<td>0.6029</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>-0.5515</td>
<td>0.9094</td>
<td>0.8776</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>-0.3612</td>
<td>0.3772</td>
<td>0.1808</td>
<td>0.3211</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VOCs</td>
<td>-0.3688</td>
<td>0.6004</td>
<td>0.5105</td>
<td>0.6139</td>
<td>0.4255</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>0.6706</td>
<td>-0.2322</td>
<td>-0.0950</td>
<td>-0.1905</td>
<td>-0.2481</td>
<td>0.0261</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RH</td>
<td>-0.6376</td>
<td>0.1835</td>
<td>0.1002</td>
<td>0.1628</td>
<td>0.3894</td>
<td>0.0702</td>
<td>-0.6859</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>WS</td>
<td>0.3289</td>
<td>-0.4139</td>
<td>-0.2450</td>
<td>-0.3701</td>
<td>-0.1831</td>
<td>-0.4004</td>
<td>0.1481</td>
<td>-0.1812</td>
</tr>
<tr>
<td>Nighttime (20:00–05:00)</td>
<td>O₃</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>-0.5636</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>-0.3424</td>
<td>0.5057</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>-0.5346</td>
<td>0.9355</td>
<td>0.7768</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>-0.2937</td>
<td>0.2138</td>
<td>0.1711</td>
<td>0.2296</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VOCs</td>
<td>-0.3093</td>
<td>0.5551</td>
<td>0.5527</td>
<td>0.6259</td>
<td>0.5430</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>0.4367</td>
<td>0.0659</td>
<td>-0.0181</td>
<td>0.0397</td>
<td>-0.2324</td>
<td>0.1296</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RH</td>
<td>-0.4026</td>
<td>-0.2231</td>
<td>-0.0086</td>
<td>-0.1684</td>
<td>0.3720</td>
<td>-0.0085</td>
<td>-0.5641</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>WS</td>
<td>0.3654</td>
<td>-0.4617</td>
<td>-0.1644</td>
<td>-0.4011</td>
<td>-0.0149</td>
<td>-0.3451</td>
<td>0.0536</td>
<td>0.1178</td>
</tr>
</tbody>
</table>

*Correlation is significant at the 0.01 level (2-tailed)

Fig. 4 – Dependence of average O₃ concentrations on wind speed at different periods of the day at YC site.

The WS during these four periods were 1.8, 1.5, 1.7 m/s, and 1.8 m/s, respectively, indicating that the WS slightly affected O₃ formation during these periods. As shown in Fig. 5, the O₃ concentration under the SE, S, and SSE directions, which were consistent with dominant direction, were the highest during EP1, EP2, and EP3 with wind frequencies of 26.2%, 28.3%, and 45.8%, respectively. NNE was the dominant wind direction during the N-EP with a wind frequency of 25.9%. In summary, increased concentrations of precursors, increased T, decreased RH, and dominant south and southeast air masses contributed to
Table 2 – Mean concentrations of pollutant and meteorological factors for three O₃ episodes and one non-episode period at YC site.

<table>
<thead>
<tr>
<th></th>
<th>O₃  (ppb)</th>
<th>NO  (ppb)</th>
<th>NO₂  (ppb)</th>
<th>NOₓ  (ppb)</th>
<th>O₃  (ppm)</th>
<th>Alkanes (ppb)</th>
<th>Alkenes (ppb)</th>
<th>Aromatics (ppb)</th>
<th>Acetylene (ppb)</th>
<th>Isoprene (ppb)</th>
<th>VOCs (ppb)</th>
<th>T (°C)</th>
<th>RH (%)</th>
<th>WS (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP1 (May 8–10)</td>
<td>67.9</td>
<td>4.1</td>
<td>21.9</td>
<td>26</td>
<td>89.9</td>
<td>0.74</td>
<td>25.6</td>
<td>7</td>
<td>3.7</td>
<td>2.2</td>
<td>46.5</td>
<td>22.9</td>
<td>50.8</td>
<td>1.8</td>
</tr>
<tr>
<td>EP2 (May 31–June 8)</td>
<td>69.6</td>
<td>4.6</td>
<td>24.2</td>
<td>28.8</td>
<td>93.7</td>
<td>0.63</td>
<td>27.6</td>
<td>11.9</td>
<td>8.4</td>
<td>4.9</td>
<td>56.3</td>
<td>29.3</td>
<td>41</td>
<td>1.5</td>
</tr>
<tr>
<td>EP3 (June 19–23)</td>
<td>60.2</td>
<td>3</td>
<td>15.7</td>
<td>18.6</td>
<td>75.8</td>
<td>0.64</td>
<td>21.67</td>
<td>4.9</td>
<td>8.0</td>
<td>2.8</td>
<td>41.4</td>
<td>28.2</td>
<td>59.6</td>
<td>1.7</td>
</tr>
<tr>
<td>N-EP (May 14–24)</td>
<td>43</td>
<td>2.5</td>
<td>15.6</td>
<td>18.1</td>
<td>58.7</td>
<td>0.62</td>
<td>22.3</td>
<td>9.3</td>
<td>5.1</td>
<td>2.6</td>
<td>40.4</td>
<td>22.3</td>
<td>74</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 5 – Wind frequency (WF) diagram of O₃ concentrations during the three O₃ episode periods (a–c) and one non-episode period (d) at YC site.

the easy formation of O₃ pollution in the central region of Zhengzhou.

2.3.2. Relative reactivity of VOCs

The concentration of VOC species and the contribution to prop-equiv and OFP during the WP are shown in Fig. S7. The results showed that the concentration can be arranged as alkanes > alkenes > aromatics > acetylene, which has good consistency with OFP, indicating that the chemical reaction activity of VOC species was closely related to the contribution of O₃ formation. The contribution of alkenes to prop-equiv and OFP reached 75.0% and 53.0%, respectively, which were higher than those of other VOC species. Following alkenes was aromatics, which contributed by 16.0% and 33.0% to prop-equiv and OFP, respectively.

Furthermore, the top 10 VOC species in terms of volume mixing ratio (VMR), prop-equiv and OFP are shown in Table S5. Some differences were observed in the top 10 VOC species of prop-equiv and OFP, but the total proportion of these 10 species were high, which were 81.8% and 71.5%,
respectively. The top 10 species from prop-equiv and OFP both included isoprene, cis-2-butene, ethene, m/p-xylene, propene, and toluene. Among the 10 VOC species that contributed the most to prop-equiv, seven alkenes and three aromatics were found, accounting for 72.5% and 9.3% of the total prop-equiv, respectively. Isoprene was the largest species in prop-equiv, which accounted for 41.9% of the total prop-equiv, followed by cis-2-butene, ethene, and styrene. For the contribution to OFP, the first three species were consistent with prop-equiv. In comparison to prop-equiv, only 4 alkenes were observed in the top 10 VOC species of OFP, which only accounted for 45.1% of the total OFP but still dominated. Although four species of aromatics were observed, their proportion was only 23.7%. In general, controlling the concentration of alkenes and aromatics in the atmosphere was effective on reducing the formation of O₃.

We also analyzed the proportion of prop-equiv and OFP for different VOC groups and the top 10 VOC species during different periods (EP1, EP2, EP3, and N-EP) as shown in Fig. 6 and Table S6. During EP1, EP2, EP3, and N-EP, the contribution of VOC groups and individual VOC species to prop-equiv and OFP were not different from the WP. For OFP, the highest contributing VOC species during EP1, EP2, and N-EP was not isoprene but cis-2-butene, accounting for 17.9%, 25.3%, and 19.3%, respectively, indicating that cis-2-butene may have an important contribution to O₃ formation. In conclusion, although the sum of alkanes and acetylene contributed a volume mixing ratio of approximately 60.0%, alkanes and acetylene contributed less than 11.0% and 15.0% to prop-equiv and OFP, respectively. This finding indicated that the concentration of VOCs and the contribution to the formation of O₃ has no obvious correlation, which required specific analysis of our specific region. Alkene (isoprene, cis-2-butene, and ethylene) and aromatic species (m/p-xylene, toluene, and styrene) contributed the most to the O₃ formation in Zhengzhou.

2.4. O₃-VOC-NOₓ relations
2.4.1. VOCs/NOₓ ratio analysis In general, if we only consider local photochemical O₃ formation, then the early morning data of VOCs/NOₓ ratios is most relevant to O₃ sensitivity analysis (Ran et al., 2009). When the ratio was lower than 10 in the morning, O₃ formation was VOC-limited, and when the value was higher than 20, NOₓ-sensitive regimes occurred. When the ratio was between 10 and 20, reducing both VOCs and NOₓ can decrease O₃ production (Hanna et al., 1996; Sillman, 1999). This simple and feasible method based on the observations of O₃ precursors have been widely used to determine the O₃ formation regime (Li et al., 2019; Prabamroong et al., 2012; Strong et al., 2013).

As shown in Fig. S8, the VOCs/NOₓ ratio at 8:00 was almost less than 20, indicating that O₃ formation (YC) was mostly in the VOC-limited and transitional regions during the observation period. In addition, to accurately identify the characteristics of O₃ formation sensitivity, we also studied the relationship between VOCs/NOₓ (ppbC/ppbv) ratio and the maximum concentration of O₃ in the early morning (6:00–9:00), noontime (11:00–14:00) and late afternoon (16:00–19:00) (Fig. 7). This method can provide more information about the sensitivity of O₃-VOC-NOₓ at differ-

---

**Fig. 6** – Fraction of VOCs species for volume mixing ratio (VMR, ppbv), Prop-Equiv (ppbC) and ozone formation potential (OFP, ppbv) for different period.
Fig. 7 – Early morning (6:00–9:00), noontime (11:00–14:00) and late afternoon (16:00–19:00) VOCs/NOx (ppbC/ppbv) ratios (a–c) and average diurnal variation of VOCs/NOx ratios (d) at YC site during the observation period.

Fig. 8 – Distribution of E(t) at ZZU, YC and GLSK sites during the whole observation period. The selected period of each day is from 06:00–18:00.

ent periods of the whole day. O₃ formation at midnight and early morning were mostly under the VOC-limited region and a few were under the transitional region. However, at high O₃ concentrations (noontime and late afternoon), the VOCs/NOx ratio was mostly close to or even exceed 20, indicating that ozone formation was more likely to be NOx-limited or in transition region control.

Fig. 7 presents the average diurnal variations of VOCs/NOx ratios and O₃ during the study period. The pattern of VOCs/NOx ratio were similar to that of O₃, reaching a maximum at approximately 14:00. O₃ formation was related not only to the concentration of precursors (especially VOCs and NOx) but also to the ratio of VOCs/NOx (Pollack et al., 2013; Sillman, 1999). In this study, the O₃ levels at 14:00 presented a slightly positive tendency with
increasing VOCs/NOx ratio at YC (Fig. S9), where the O3 formation shifted to the transition control region and may even be sensitive to NOx when high O3 levels were observed. This finding is similar to the observations in Shanghai (Gao et al., 2017) and Hangzhou (Li et al., 2017b) and attributable to the increased O3 production efficiency at high VOCs/NOx, if the advection of the air mass is not considered.

2.4.2. SPM
The above-mentioned oversimplified VOCs/NOx ratio method have the following limitations: (1) the empirical threshold values of 10 and 20 may not be suitable for all region; (2) the method did not consider the diffusion of regional pollutant; and (3) considering that only 56 VOC species (most of which are anthropogenic) were included in this study, the VOCs/NOx ratio may be underestimated. Based on the trace gas (O3, NO, and NO2) data at ZZU, YC, and GLSK, we used SPM as another alternative analysis about ozone formation sensitivity.

The data distribution of E(t) at ZZU, YC, and GLSK during the whole observation period are shown in Fig. 8, which showed that 90.0% of the E(t) at three sites were less than 0.9, and the mean value was less than 0.6, indicating that the three sites have similar O3 formation sensitivities under VOCs-limited and transition control region. As shown in Fig. 9, during the 61-day observation period, 36, 40, and 29 days at ZZU, YC, and GLSK had reaction extent values $E(t) < 0.6$; and 24, 20, and 31 days had $0.6 < E(t) < 0.9$. However, the number of days when the $E > 0.9$ were
only 2, 1, and 1, which also indicated that the O₃ formation at the three sites during the observation period was almost always under the VOC-limited and transition control regions alternately. Besides, O₃ episode periods (EP1, EP2, and EP3) showed different O₃–VOC–NOₓ sensitivity relationships compared with O₃ N-EP, as shown in Fig. 9. O₃ formation during EP1, EP2, and EP3 were under the transition control region, whereas during N-EP, O₃ formation was controlled by VOCs. The O₃ sensitivity varied with different periods, indicating the complexity of O₃ formation in Zhengzhou.

For the daytime, the mean profiles of E(t) and O₃ concentration in ZZU, YC, and GLSK are shown in Fig. 10. The trend between E(t) and O₃ level at the three sites was consistent, and the maximum value was recorded at 15:00. In addition, Fig. S10 shows that the correlation of O₃₁₈–max (maximum hourly ozone concentration during 06:00–18:00) and Emax at the three stations was high, and the correlation coefficients were 0.961, 0.974, and 0.965. This finding may be due to the increased production of actual photochemical smog as the O₃ concentration increased; then, E value increases.

We also compared the O₃ formation sensitivity of YC based on the VOCs/NOₓ ratio and the SPM method (Table 3). We determined that 29 days were under the VOC-limited region, and the consistency between the conclu-
sions of both SPM and VOCs/NOx ratio were reached 73.7%; 10 days were determined as transition control area with the consistency of 50.0%–52.6%. Some differences (only three days were under NOx-limited) were observed in the NOx-limited results obtained via the two methods, but it also indirectly showed that O3 formation at YC was almost always in the VOCs-limited and transition control regions. The difference between the two methods may be due to the uncertainty of the evaluation criteria. The uncertainty of SPM mainly lies in the concentration of pollutants, the selection of empirical parameters and the estimation of pollutant deposition (Blanchard et al., 1999).

We compared the studies using different methods to evaluate the O3–VOC–NOx sensitivity in China (Table 4). Results indicated that urban areas tend to be under the control of VOCs, although which was different from our conclusion on Zhengzhou, the finding of Zhengzhou were consistent with Li et al. (2017b). Furthermore, the most dominant contributors of O3 formation in majority regions were reactive alkenes and aromatics, which were consistent with the results of O3 formation analysis (alkene and aromatic contributed 53.0%–75.0% and 16.0%–33.0%) in this research. Hence, for a reduced O3 in Zhengzhou, active alkenes, aromatics (especially isoprene and m/p-xylene), and NOx, should be synergistically reduced rather than reducing VOCs alone.

3. Summary and conclusions

In this study, we studied O3 and its precursors, CO, NO, NO2, VOCs and H2O2 at three sites in the Zhengzhou area from May 1 to June 30, 2018, along with meteorological data. During the early summer season, comparatively high O3 levels were observed in Zhengzhou at central China. During the whole observation period, the observed O3 levels and the rates of O3 concentration exceeded Chinese National Air Quality Standard Grade II (99.3 ppbv) at the three sites presented relatively good consistency, showing that O3 pollution in Zhengzhou is a regional characteristic, which needs concerted regional reduction.

For the site at the urban area, four periods (three O3 episode periods and one non-episode period) were further contrasted. The results indicated that high concentration of precursors, high temperatures, low relative humidity and moderately high wind speed can cause O3 episodes. Meanwhile, the study not only confirmed the high correlation between the transportation of SSE direction and the O3 pollution events in the upwind region, but also found that the transportation of south and southeast direction also contributed to the O3 pollution events.

The alkenes were the most chemically active species, accounting for 75.2% of prop-equiv, followed by aromatics (15.6%), alkanes (8.7%), and acetylene (0.4%). The OFF results demonstrated that alkenes contributed the most to O3 formation, accounting for 52.9% of OFF, followed by aromatics (23.9%), alkanes (13.3%), and acetylene (0.9%). Isoprene was the largest species in terms of prop-equiv and OFF during the whole period, accounting for 41.9% and 18.7%, respectively. In addition, based on the comparison of OFF and prop-equiv at different periods, cis-2-butene also remarkably contributed to O3 formation. Alkenes contributed the most to O3 formation, whose emission reduction should be first carried out and simultaneous mitigation of aromatics and NOx will be more effective.

Based on the VOCs/NOx ratio and SPM, the O3–VOC–NOx relationship demonstrated that O3 formation was mainly under either the VOC-limited or transition control region in Zhengzhou during early summer. High episode of O3 formation is more likely to occur under the transition control region. However, the above conclusions are only based on observational analysis without any modeling research. Furthermore, source appointment research based on the model should be conducted to determine more exact and efficient emission control.

Declaration of Competing Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (No. 2017YFC0212403).

Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.06.021.

REFERENCES


