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Enhancement of ozone formation by increased vehicles emission and reduced coal combustion emission in Taiyuan, a traditional industrial city in northern China

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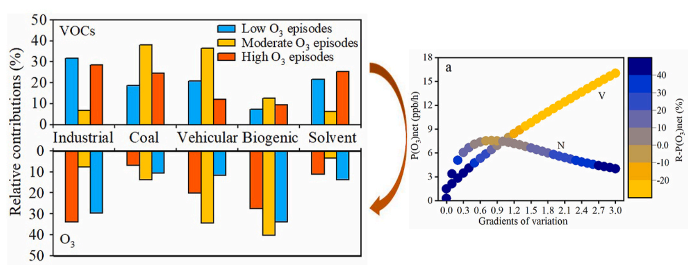
HIGHLIGHTS

- The highest VOCs level was detected at the traffic-intensive site in Taiyuan.
- VOCs limited regime of summertime O_3 formation in Taiyuan.
- Vehicles and industries contributed more to O_3 than other anthropogenic sources.
- Vehicular emissions will become more remarkable in traditional industrial cities.

GRAPHICAL ABSTRACT



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ABSTRACT

Coal combustion and industrial processes were often the main sources of atmospheric pollutants in traditional industrial cities in northern China. Studies on sensitivity analysis and source apportionment of ozone formation, which are the basis of ozone pollution controlling, are limited in those cities. The systematic observations of ambient Volatile Organic Compounds (VOCs) were performed to better investigate the major anthropogenic sources of summertime O_3 during different O_3 episodes in Taiyuan, a traditional industrial city in northern China. Average mixing ratio of VOCs was 21.80 ppbv during the summer sampling period, and the highest value was measured at the traffic-intensive area. Source apportionment carried by positive matrix factorization model (PMF) showed that VOCs from vehicular emissions exceeded those from coal combustion, and their contributions to the total ambient VOCs were 28.12% and 25.95%, respectively. VOCs limited regime of summertime O_3 formation was revealed by using a photochemistry model. Alkenes group was the most crucial contributor to O_3 formation. Vehicular emissions made the largest anthropogenic contribution (25.35%) to total O_3 formation, while industrial processes with the contribution of 29.81% to O_3 was also unacceptable in high O_3 episodes. Multi-sources joint prevention and control, especially the joint of vehicular emissions and industrial processes

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emissions, may effectively reduce the summertime O_3 pollution in Taiyuan. Given the vigorous implementation of the coal reform policies and future economic and energy restructuring, effects of vehicular emissions on VOCs and summertime O_3 should become more remarkable, indicating that the implementation of more stringent control strategies of vehicular emissions may be the key to alleviate O_3 pollution in traditional industrial cities in the future.

1. Introduction

Tropospheric O_3, the main component of photochemical smog, is generated by volatile organic compounds (VOCs) and nitrogen oxides (NO*x*) in the presence of sunlight. It has become a pollutant of much concern in most Chinese metropolises, given its increasing concentration and negative effects on air quality during summertime (Li et al., 2017; Ma et al., 2016; Xue et al., 2014; Zhao et al., 2020). In 2018, the 90th percentile of the daily maximum 8-h average for surface O_3 reached at 96 ppbv in 169 major Chinese cities, and 63.3% of these 169 cities were characterized as being polluted by O_3 (MEE, 2017). Persistent O_3 pollution is extremely harmful to human health and hampers ecologically sustainable development (Dolker and Agrawal, 2019; Gao et al., 2020; Hu et al., 2020; Malley et al., 2017). Therefore, taking effective measures to alleviate O_3 pollution are imminent.

As precursor to O_3 pollution, VOCs play a crucial role in tropospheric O_3 formation and have been extensively studied. Positive matrix factorization (PMF) model is a reliable method that has been widely employed to identify sources of VOCs (Gao et al., 2020; Li et al., 2019; Liu et al., 2016, 2019b; Yan et al., 2017a). The relative contribution of sources to ambient VOCs in different cities is unique, given various factors such as the diversity of the energy structures and industry distribution. Localized source apportionment of VOCs is essential, as the major sources of O_3 production can be estimated through these VOCs results (Wu and Xie, 2017). Unfortunately, the relationship between O_3 formation and its precursors is highly nonlinear in the actual photochemical process (Liu et al., 2012; Zhong et al., 2017), which complicates our understanding of the effects of VOCs on O_3 formation and identification the major sources of O_3 based on observations of VOCs.

VOCs contribute to O_3 formation by participating in a series of chemical reactions, and this process have been simulated well by box model, such as the observation-based model (OBM) (Wang et al., 2017), National Center for Atmospheric Research (NCAR) Master Mechanism model (Liu et al., 2019a), photochemical box model with master chemical mechanism (PBM-MCM) (He et al., 2019; Wang et al., 2018; Zeng et al., 2018). And limited researches have used the receptor model coupled with box model to identify the sources of O_3.

Taiyuan, one of a traditional industrial city in northern China, is an important base of energy, chemical and heavy industries in China. Previous studies have indicated that coal-related emissions such as coal combustion have been the main sources of atmospheric pollutants in Taiyuan (Yan et al., 2017b). It has been facing severe O_3 pollution, especially in summer, for a considerable time period. Past observations in Taiyuan for 2018 showed that the 90th percentile of the daily maximum 8-h average O_3 mixing ratio (108 ppbv) exceeded 3.24% of the value in 2017 (Ecological and Environment Bureau of Taiyuan, 2018). O_3 has thus become one of the biggest air pollutants in Taiyuan. However, to date, no systematic observation of ambient VOCs in Taiyuan has been performed. Therefore, monitoring of the VOCs mixing ratio and identification of the major sources of O_3 formation based on observations are crucial for Taiyuan.

This study, involved a VOCs measurement field campaign to analyze the characteristics and major sources of VOCs in Taiyuan during different O_3 episodes. Photochemistry model with the specific Master Chemical Mechanism (MCM v3.3.1) was coupled with the PMF model to assess the effects of VOCs on O_3 formation. It attempts to provide guidance for future research and assist the local government, especially for the traditional industrial city in northern China, to make strategic decisions on VOCs and O_3 reduction in summertime.

2. Materials and methods

2.1. Site description

This study concentrated on the urban area of Taiyuan (Fig. S1). According to the topographic conditions and functional zones of Taiyuan, sites SL, TY, XD, and JY were selected to perform online observations of trace gases, including O_3, NO, NO_2, CO, and conduct field sampling of VOCs. The sampling positions were set on rooftops at approximately 10 m–22 m from the ground. Fig. S1 presents the locations of the sampling sites and the surrounding environment. Thermal power plants and steel plants are likely to be the biggest emission sources in the urban area of Taiyuan. The steel plant located between sites SL and TY, has an annual design output capacity of 12 million t, including 4.5 million t of stainless steel, and is a global leader in the stainless steel industry. Site TY, is located in a traffic-intensive area, surrounded by main roads in the east and south. XD site is a typical mixed area of residential and traffic with a large population and traffic flow. While more industries, such as coking plans and thermal power plants, are distributed in the south of JY site.

2.2. Field sampling

The samples of VOCs were simultaneous captured at four sampling sites for 2–7 days from May to July in 2016 using stainless SUMMA canisters (3.2L Silonite® Canisters, Entech Instruments Inc., CA, USA), which were pre-cleaned with high purity nitrogen and evacuated to vacuum, equipped with a restricted sampler (39-RS-4, Entech Instruments Inc., CA, USA). The selected sampling days should consider the continuous stable meteorological and rainless weather. Conventional and intensive observation were carried out with the frequency of 1 sample per hour. In the daytime, sampling was carried out simultaneously at four sites, and the average mixing ratio of VOCs observed at these sites can roughly represent ambient VOCs level in Taiyuan during the observation period. Additionally, TY site, located in the center of Taiyuan, can better reflect the situation of Taiyuan urban area. To understand the diurnal variation of ambient VOCs in Taiyuan, the daytime and nocturnal samples were collected at TY site during the intensive observation period. The detailed sampling information were listed in Table S1. A total of 265 valid samples were collected after excluding that affected by rainfall.

2.3. Chemical analysis

The Model 7100 preconcentrator (Entech Instruments Inc., USA) coupled with a gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent 7890A/5975C, USA) were used to detect the compounds of VOCs samples. Detailed description of the analytical method can be found in previous study (Yan et al., 2016, 2017a). Trace gases (O_3, NO, NO_2, CO) were simultaneously sampled online with 1h resolution during the observation period. We briefly described the measurement and quality control and quality assurance in Text S1& Text S2.

2.4. Model description

2.4.1. Photochemistry model description

Based on the observed data, the actual atmospheric photochemical processes and generation of O_3 can be simulated via the Framework for Zero-dimensional (0-D) Atmosphere Modeling(F0AM) (Kim et al., 2013; Wolfe et al., 2016). Thus, we believed that the combination of the photochemistry model and the PMF method (details were given in Text S3) will provide significant source-related information concerning O_3 formation and help improve prevention and control of regional O_3 pollution. This combination has not yet been tested toward quantifying of O_3 sources before.

The mixing ratio of quantified VOCs species, trace gases (i.e., CO, NO, NO_2, and O_3), and three meteorological parameters (pressure, relative humidity (RH) and temperature (T)) corresponding to the VOCs samples were used to constrain the model in this study. Solar zenith angles were calculated using functions of time and location following (Ibrahim and Afshin, 2004). Photolysis frequencies (*JO^1D (J1), JNO_2 (J4)*) were derived from the NCAR's Tropospheric Ultraviolet and Visible radiation model (TUV v5.3, available at http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/) and the other parameters relevant to this study (O_3 column, surface albedo, cloud optical depth, aerosol optical depth, and single scattering albedo) were obtained from https://worldview.earthdata.nasa.gov/. The no explicit input J-values were calculated using the TUV/HYBRID method, which has been recommended for most "real atmosphere" simulations (Wolfe et al., 2016) and the values were scaled by setting the correction factor (jcorr) to the average of *J1* and *J4*. The integration time for each step was set to 3600 s for the photochemical model running. While timestamp was set to the time series of VOCs, ensuring the same base for both model and observation in this study.

The zero-dimensional photochemistry model based on the Master Chemical Mechanism version 3.3.1 were applied to simulate the chemical rates of target species. Note that the horizontal and vertical transport processes were ignored in the model. Then, the chemical rates (*R[X]*) of each species *X* were calculated using Eq. (1).

$$R[X] = \sum_{i=1}^{n} f_i^X k_i G_i \quad (1)$$

Where f_i^X is the stoichiometric constants of each reactant species for given reaction *i*. k_i is the rate constants for given reaction *i*. G_i is the product of reactant mixing ratios for specific reaction *i*. *n* is the Integer index for G_i. Generally speaking, the net O_3 production rate ($P(O_3)$net) was roughly equivalent to the chemical rates of destroy NO and peroxy radical (XO_2: RO_2 and HO_2) to formation NO_2. The stoichiometric constants of NO and XO_2 are −1 while that of NO_2 is 1.

Dilution is parameterized by Eq. (2).

$$\frac{d[X]}{dt} = k_{dil}\left([X]_b - [X]\right) \quad (2)$$

Where k_{dil} is the 1st-order dilution rate constant which is set as 1/86400 s in this study (Wolfe et al., 2016). $[X]_b$ is a fixed background concentration.

2.4.2. O_3 production simulation

Based on the chemical rates (*R[X]*) of each species *X*, the $P(O_3)$net can be calculated by Eq. (3) (Cardelino and Chameides, 1995; Carter and Atkinson, 1989).

$$P(O_3)net = sum(R[NO_2], R[NO], R[XO_2], d[X]/dt) \quad (3)$$

Two scenarios were set to quantitatively analyze the VOCs groups or sources influencing O_3 formation. While the original scenario employed the observed data, the data for the controlled scenario were selected assuming that the specific VOCs group or source was disregarded. The divergence of $P(O_3)$net in the two scenarios was roughly equal to $P(O_3)$net of the controlled group or source.

The relative incremental reactivity (*RIR*) was represented by the $P(O_3)$net variation ratio resulting from the change in the emission ratio (Cardelino and Chameides, 1995).

$$RIR^S(X) = \frac{[P(O_3)net(X) - P(O_3)net(X - \Delta X)]/P(O_3)net(X)}{\Delta S(X)/S(X)} \quad (4)$$

Where $P(O_3)$net(X) represents the $P(O_3)$net of a specific species *X*, group *X*, or source *X*. $P(O_3)$net *(X−ΔX)* refers to $P(O_3)$net of *X* caused by the hypothetical emission change *ΔX*. *S(X)* is the total observed mixing ratio of precursor *X*. *ΔS(X)* is the total mixing ratio change of precursor *X* caused by the hypothetical emission change (assumed to be 20% in this study).

Average RIR of VOCs groups or sources can be calculated by Eq. (5) (He et al., 2019; Zeng et al., 2016).

$$\overline{RIR}(X) = \sum_1^n [RIR(X) \times P(O_3)net] \Big/ \sum_1^n P(O_3)net \quad (5)$$

Where *n* is the number of samples simulated.

The contribution of the VOCs to O_3 formation is calculated by Eq. (6).

$$Contribution(X) = \overline{RIR}(X) \times Con(X) \Big/ \sum_{i=1}^m [\overline{RIR}(X) \times Con(X)] \quad (6)$$

Where *Con(X)* is the average mixing ratio of group *X* or source *X* derived from PMF. *m* is the number of VOCs groups or factors (or sources) resolved by PMF, respectively.

3. Results and discussion

3.1. General features of O_3 and its precursors

The time range of this study spanned May to July in 2016, and included temporary high O_3 episodes (maximum hourly O_3: 109 ppbv, in June), moderate O_3 episodes (maximum hourly O_3: 95 ppbv, in July) and low O_3 episodes (maximum hourly O_3: 68 ppbv, in May and June) (Table S3). The average wind speed was relatively low at 2 m/s, the prevailing direction being southern. Obvious diurnal variations in T and RH were observed. The maximum T (35 °C) and the low RH (14%) often occurred at noon, and these conditions are well-known as being favorable for photochemical reactions (Zhao et al., 2020). The average T and RH were 25 °C and 56% during the whole monitoring period.

Fig. 1 demonstrates the time series for the average mixing ratios of O_3, NO, NO_2, and the meteorological parameters at the four sites. The mixing ratio of NO was continuously low until midnight and reached its highest value in the early morning after beginning to increase at midnight. This observation indicates that strong local emissions of NO were rapidly oxidized to NO_2. The NO_2 mixing ratio decreased after sunrise and gradually rose in the afternoon. The trend of the O_3 mixing ratio was opposite to that of NO_2 and showed obvious photochemical reaction characteristics in the daytime. This phenomenon demonstrated that NO_2 was consumed during a photochemical reaction to produce O_3, and accumulated as a result of the weaken photochemical reactions in the afternoon. The temporary peak value of O_3 often occurred at noon, and exceeded the Grade II national air quality standard (100 ppbv), thus indicating distinctly high O_3 episodes. Therefore, it would be logical to conclude that the O_3 observed during daytime in Taiyuan can be attributed mainly to photochemical reactions.

The quantified 47 VOCs species included 26 alkanes, 10 alkenes, 10 aromatics, and 1 alkyne. As show in Table S3, the mixing ratio of VOCs ranged between 16.97 and 24.79 ppbv at the four sites, and the highest value was detected at site TY. It may be primarily attributed to the severe traffic jams at site TY. Overall, the average mixing ratio of total VOCs was 21.80 ppbv, namely 10.93, 4.64, 3.56, and 2.67 ppbv for

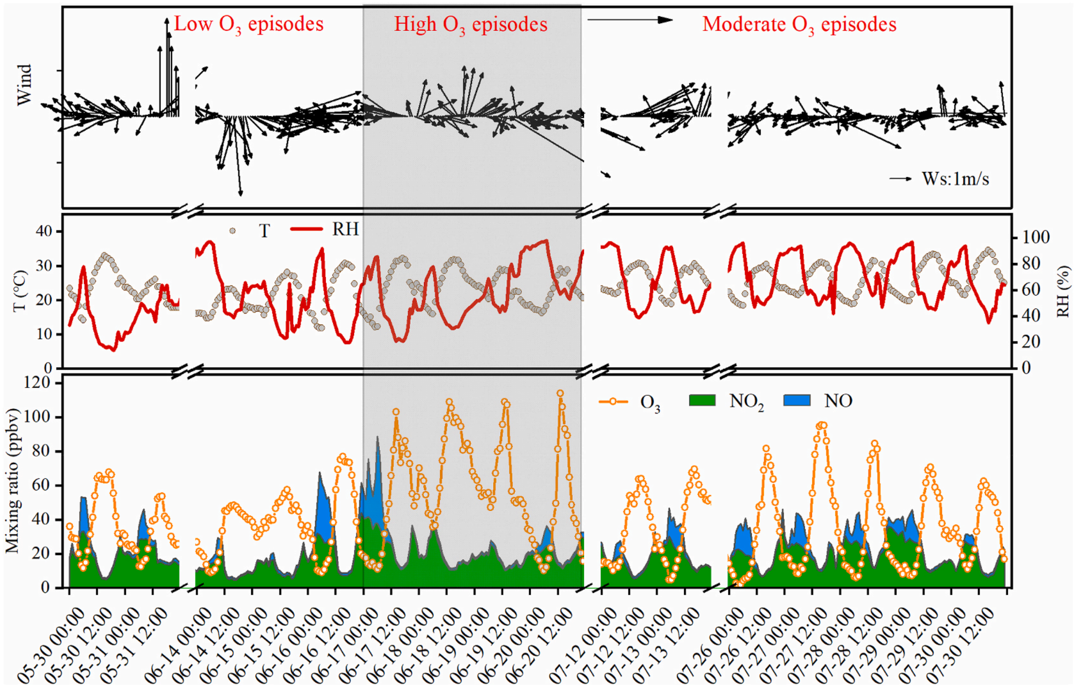

Fig. 1. Time series for the average mixing ratios of O_3, NO, NO_2, and the meteorological parameters.

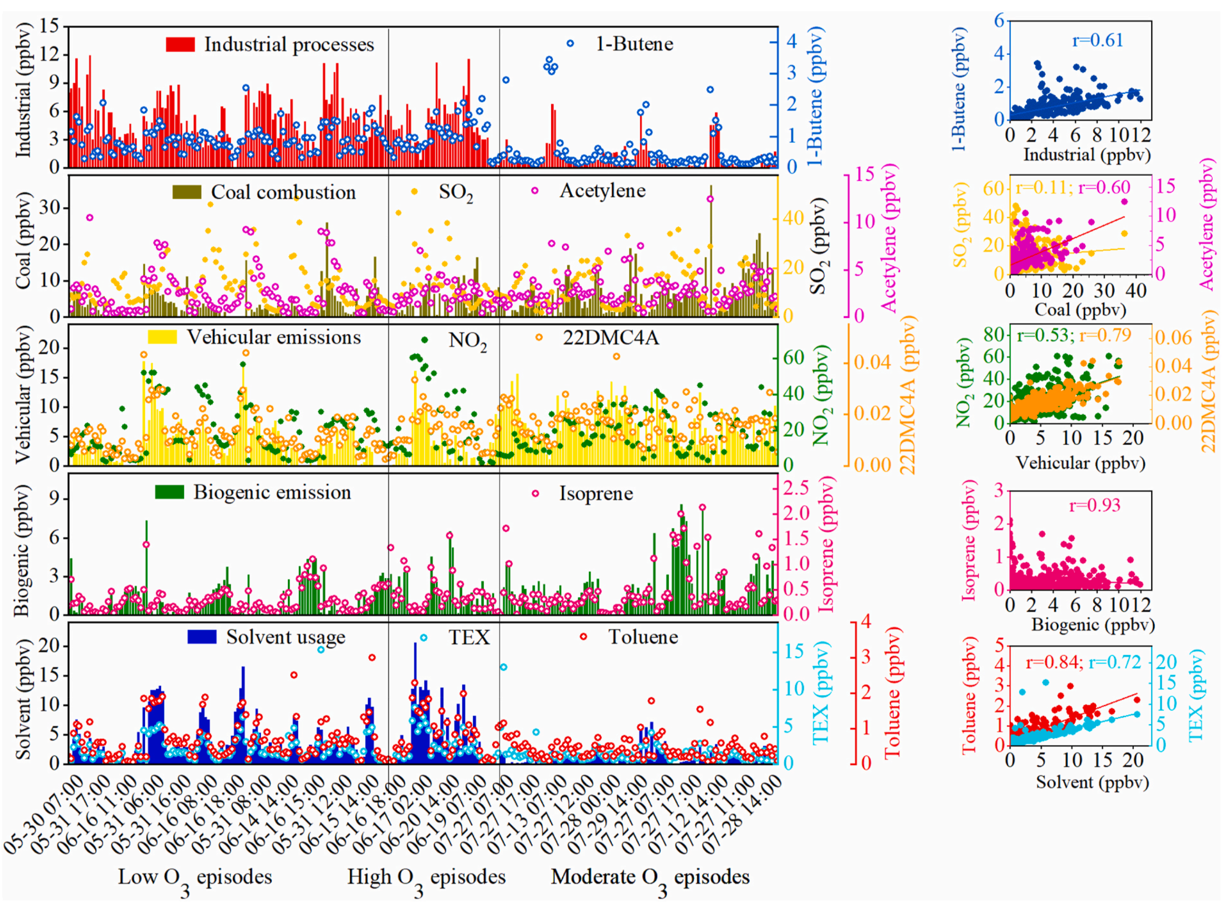

Fig. 2. Time series of the factors extracted from PMF and their tracers, including SO_2, NO_2, 1-Butene, Acetylene, 2,2-dimethybutane(22DDMC4A), Isoprene, TEX (Toluene & Ethylbenzene & Xylene) and Toluene, and correlations between these tracers and PMF-derived source.(The horizontal coordinate scale is arranged in accordance with the monitoring schedule of VOCs at SL, TY, XD, and JY site during different O_3 episodes.)

alkanes, alkenes, aromatics, and alkyne, respectively. The results indicated that alkanes (50.14%) were the most abundant VOCs in Taiyuan during summer, consistent with the results reported for most Chinese cities (Table S4) (He et al., 2019; Hui et al., 2018; Li et al., 2015, 2019; Liu et al., 2016, 2019b; Tang et al., 2009; Zhang et al., 2019; Zhu et al., 2016). This finding may be related not only to the emission intensity, but also to the accumulation caused by the weak chemical reactivity of alkanes. As a typical coal-based city, the concentration of alkyne (the tracers of coal combustion (Liu et al., 2008)) was found to be higher than that in the other cities listed in Table S4, except for Zhengzhou (Li et al., 2019, 3.8 ppbv) and the Pearl River Delta (He et al., 2019,3.4 ppbv). The averaged VOCs levels in Taiyuan were similar to that in Beijing-Tianjin-Hebei (Li et al., 2015; Liu et al., 2016, 19.8–23.3 ppbv), Guilin (Zhang et al., 2019, 21.8 ppbv) and Shanghai (Liu et al., 2019b, 23.8 ppbv). The overall level of VOCs was much higher than that in Wuhan (Hui et al., 2018, 15.9 ppbv), the North China Plain (Zhu et al., 2016, 11.4 ppbv), and background areas (Tang et al., 2009, 3.7–16.6 ppbv). However, it was much lower than that in Zhengzhou (Li et al., 2019, 29.2 ppbv) and the Pearl River Delta region (Guo et al., 2017; He et al., 2019, 34.8 ppbv). The total VOCs in Taiyuan was at a medium level among these referenced cities.

3.2. Source apportionment of VOCs

To identify the main sources of the VOCs, a total of 265 valid samples were collected from the four sites and 46 VOCs were utilized for the PMF analysis in this study. Running results and corresponding source profiles extracted by the PMF were presented in Fig. S3. Five factors were identified after 20 runs: industrial processes, coal combustion, vehicular emissions, biogenic emission, and solvent usage sources. Time series of these factors were basically consistent with their corresponding indicator compounds and positively correlated between of them with higher correlation coefficients (r > 0.60) through the Pearson correlation analysis (Fig. 2.). For example, factor 3 was significantly correlated with NO_2 (r = 0.53) and 2,2-dimethybutane (r = 0.79), confirming the identity of the vehicular emissions source. Detailed identification information of PMF factors was explained in Text S4.

As shown in Fig. 3, vehicular emissions (28.12%) and coal combustion (25.95%) were the major contributors of ambient VOCs during the total observation period. The contributions of industrial processes, solvent usage, and biogenic emissions to ambient VOCs were 19.77%, 17.23%, and 8.94%, respectively. Industrial processes were the largest contributor (31.68%) of ambient VOCs, followed by solvent usage (21.55%), vehicular emissions (20.91%), coal combustion (18.65%), and biogenic emissions (7.22%) during the low O_3 episodes. The proportions of coal combustion (37.97%) and vehicular emissions (36.41%) ascended sharply in the moderate O_3 episodes, however, the contributions of industrial processes (28.48%), solvent usage (25.40%), and coal combustion (24.57%) were higher in the high O_3 episodes compared to those in the low O_3 episodes.

The contribution of vehicular emissions to VOCs exceeded those from coal combustion in Taiyuan. This result was attributed to economic development and the reductions in coal combustion emissions. With the gradual shift of coal to gas, coal to electric energy, and clean energy substitutions in Taiyuan, the coal consumption dropped by 4.3 million t in 2017 (Ecological and Environment Bureau of Taiyuan, 2018) and 0.56 million t in 2018 (Ecological and Environment Bureau of Taiyuan, 2019). The contribution of coal combustion is expected to decrease with the future energy readjustments. For industrial processes, the country is making persistent efforts to control its emissions in many industrial cities, including adjustment of industrial structure, cleaner production, process optimization, and so on. Although industrial processes made the most contribution (31.68% and 28.48%) during the low and high O_3 episodes, VOCs emitted by this source is expected to decrease in Taiyuan. However, the number of privately owned cars has also increased with the economic development, growing by as much as 53% from 2014 to 2018. As a consequence, High contribution of vehicular emission to ambient VOCs is predictable, which may also be a common feature in many traditional industrial cities in northern China, and controlling the emission from this source will be a long-term and effective measures to reduce ambient VOCs.

The relative contribution of the five major sources to the ambient VOCs varied in different O_3-level episodes, which may be primarily attributed to the meteorological conditions and the distribution of pollution sources. As shown in Fig. S4, the contribution of vehicular emissions and solvent usage to ambient VOCs can be characterized by localization while other anthropogenic sources, including coal combustion and industrial processes, increase the ambient VOCs level through regional transportation. High contribution of industrial processes from north and south direction to ambient VOCs occurred under strong wind situation (wind speed >3 m/s) in the low O_3 episodes. While in the moderate O_3 episodes, vehicular emission and coal combustion from south direction were the two largest contributors occurred under weak wind situation (wind speed <2 m/s) and the wind speed above 3 m/s, respectively. Therefore, controlling the VOCs from vehicular emissions together with the restrictions imposed on coal will reduce the VOCs mixing ratios during moderate O_3 episodes. Compared with low and moderate O_3 episodes, it had the characteristics with high contributions both local and regional sources to ambient VOCs during high O_3 episodes. More stringent strategies should be taken to reduce ambient VOCs level in this period. Most of the industries, including coking plants, iron and steel plants, and chemical factories, are relocated outside the urban area, the VOCs emitted from the industrial processes can still be transported and accumulate in urban aera of Taiyuan. Moreover, domestic solvent use, including paint application, dry cleaning, solvent evaporation from household products, and so on, may be the important sector for VOCs. The volatilization of solvents usage in the iron and steel manufacture process and packing and printing at factories located near

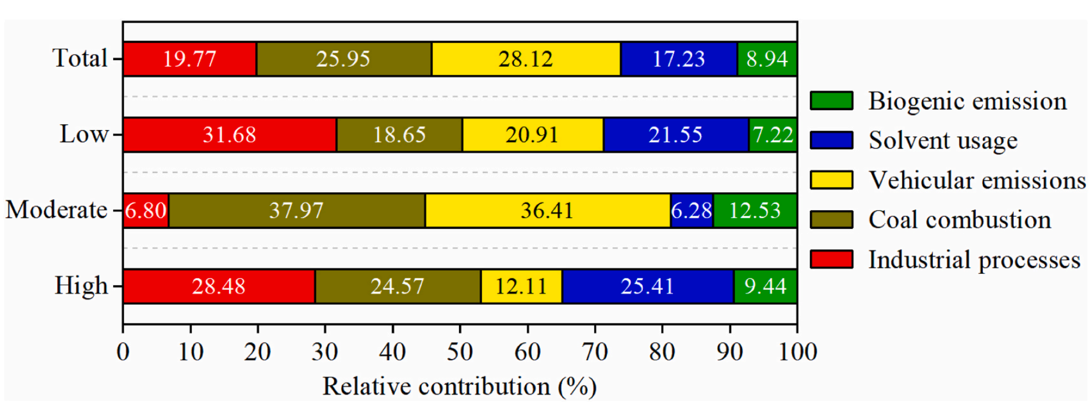

Fig. 3. Source contributions to ambient VOCs at different O_3-level episodes in Taiyuan.

sites TY and XD site also probably contributed to the total VOCs. But policies of improving solvent quality or water-based substitution have been performed, and the influence of solvent usage on VOCs is expected to be weaken in Taiyuan. Therefore, restricting emissions from industrial processes and vehicles was the key to reduce the ambient VOCs level during the high O_3 episodes.

3.3. Simulated effects of VOCs on O_3 production

3.3.1. Sensitivity tests of O_3 generation

O_3 generation was affected by the concentration of its precursors (NO*x* and VOCs). In this study, the VOCs mixing ratio of each daytime sample and the corresponding NO*x* concentration were inputted as the initial concentration. Detailed model validation was shown in Text S5, and good agreement between the simulated and observed O_3 tendency were achieved by the photochemistry model (Fig. S5). Then the VOCs and NO*x* mixing ratios were changed at a gradient of 0.1 between 0 and 3 (corresponding with the decrease in the initial VOCs and NO*x* concentrations from 100% to −200%) to obtain $P(O_3)$net under different reduction gradients. The main sensitive factor affecting O_3 generation can be roughly judged by the reduction in average $P(O_3)$net with the variation in the precursors.

Fig. 4 shows the proportion of the variation in $P(O_3)$net with the changes in NO*x* and the VOCs. $P(O_3)$net changes distinctly with the variation in the VOCs (Fig. 4a). $P(O_3)$net decreased slowly with the reduction between 30% and 100% of NO*x* (corresponding with the variation range between 0.7 and 0), while NO*x* increment may cause the opposite effect. Additionally, the variation percentages of $P(O_3)$net with the change in NO*x* were far lower than those caused by the variation in VOCs. For instance, the proportion of reduction in $P(O_3)$net was 36.54% when the VOCs were reduced by 0.5 (50%), while the corresponding value was only 4.74% when NO*x* was cut by 0.5 (50%). This phenomenon evidently indicates the VOCs limited regime of summertime O_3 generation in Taiyuan. Thus, it was concluded that O_3 generation via photochemistry can be effectively reduced by controlling VOCs in Taiyuan.

To analyze the sensitivity of O_3 generation from the perspective of VOCs groups, alkanes, alkenes, aromatics, and alkyne concentration were reduced using the same gradients as the total VOCs. As shown in (Fig. 4b), $P(O_3)$net ranged between 2.83 and 7.07 ppb/h when the alkenes mixing ratio was reduced from 0 to 0.1. Average $P(O_3)$net ascended sharply with the alkenes increase in the alkenes concentration, while it changed slowly for variations in the other three groups. This clearly indicates that the alkenes group was the most sensitive factor for O_3 generation, and thus, more attention should be paid to components with alkenes in Taiyuan.

3.3.2. Effect of VOCs on O_3 photochemical production

As shown in Fig. 5, average $P(O_3)$net was 5.04 ppb/h during the overall observation period, including the low, moderate, and high O_3 episodes, and the corresponding average $P(O_3)$net values amounted to 3.11, 6.44, and 6.67 ppb/h, respectively. The average level of O_3 were 59.56 and 43.42 ppbv during the high O_3 episodes and overall observation period, respectively. The meteorological parameters in the moderate O_3 episodes (T: 28 °C and RH: 61%) and the high O_3 episodes (T: 26 °C and RH: 52%) were more conducive to O_3 formation than those in the low O_3 episodes (T: 23 °C and RH: 43%). Moreover, $P(O_3)$net was consistent with the O_3 levels during different O_3 episodes, which indicates that the level of O_3 precursors were sufficient to cause summertime O_3 pollution via local photochemical reactions under the suitable meteorological conditions.

In addition, although the mixing ratio of the alkenes group was lower, its average $P(O_3)$net value were considerably high at 2.42, 5.47, and 5.17 ppb/h in the low, moderate, and high O_3 episodes, respectively (Fig. 5a & b). Fig. 5c shows the relative contribution of the VOCs groups to O_3 production. These results show that the total contribution of alkenes exceeded 75%, thus pointing to the highest effect on O_3 production. The relatively lower O_3 production rate or reaction activity of alkanes translated into low impact on O_3 generation although the emission intensity of alkanes was relatively high. Therefore, it is necessary to simultaneously consider the O_3 production rate and the mixing ratio of ambient VOCs so that the sensitivity components of photochemical O_3 formation can be ascertained accurately. This aspect is crucial to alleviate photochemical pollution in Taiyuan.

3.3.3. Effects of VOCs sources on O_3 photochemical formation

It is necessary to further clarify the effects of the VOCs sources on O_3 photochemical formation in order to develop precise strategies for O_3 reduction, as summertime O_3 generation in Taiyuan is explicitly attributed to VOCs. To achieve this end, we simulated $P(O_3)$net of the VOCs sources extracted from the PMF. As shown in Fig. 6., the results showed that biogenic sources were the first contributor toward the chemical reaction capacity required to generate O_3 during the whole observation period, as well as low, moderate, and high O_3 episodes (1.55, 0.87, 2.18, and 2.17 ppb/h, respectively). These findings were consistent with the previous conclusion (Kim et al., 2013). Considering the uncontrollability of biogenic sources, the effects of anthropogenic VOCs sources on summertime O_3 formation were considered as the key targets in this study. Vehicular emissions (average $P(O_3)$net: 0.80 ppb/h) were the largest active anthropogenic source for O_3 production, followed by industrial processes (0.78 ppb/h), coal combustion (0.52 ppb/h), and solvent usage (0.33 ppb/h) (Fig. 6(d)), suggesting that VOCs emitted from vehicular emissions and industrial processes play crucial roles in O_3 formation during summertime in Taiyuan. More attention should thus be devoted to the effects of vehicular emissions and industrial processes on O_3 production due to their relatively high $P(O_3)$net values.

Fig. 6 summarizes the relative contribution of each anthropogenic

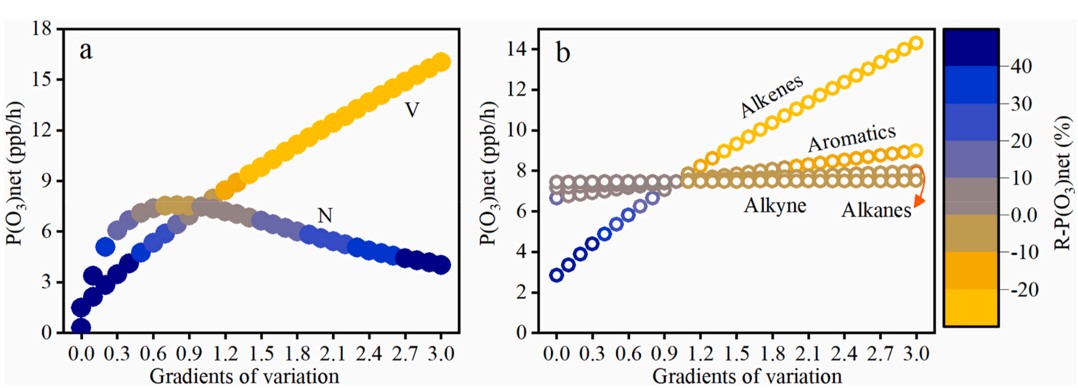

Fig. 4. Sensitivity tests of O_3 production to NO*x* (N), VOCs (V) (a), and groups colored by the reduction proportion of $P(O_3)$net variation(R–$P(O_3)$net) (b).

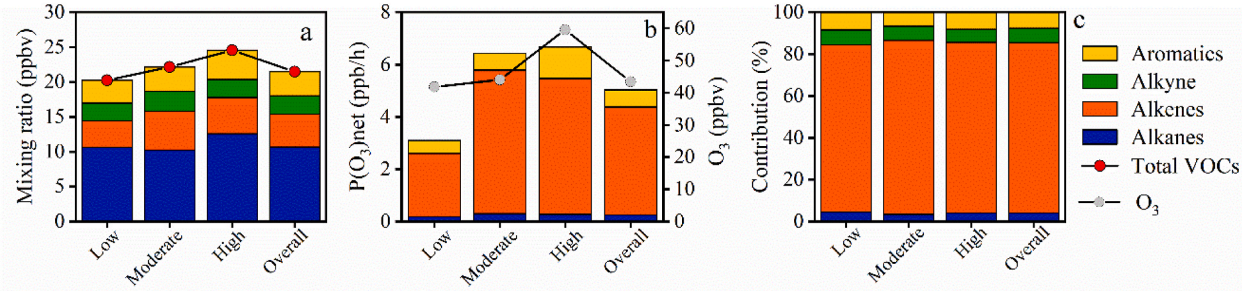

Fig. 5. Mixing ratios(a), P(O_3)net values(b), and contributions to O_3 production (c) of the four groups during different O_3 episodes.

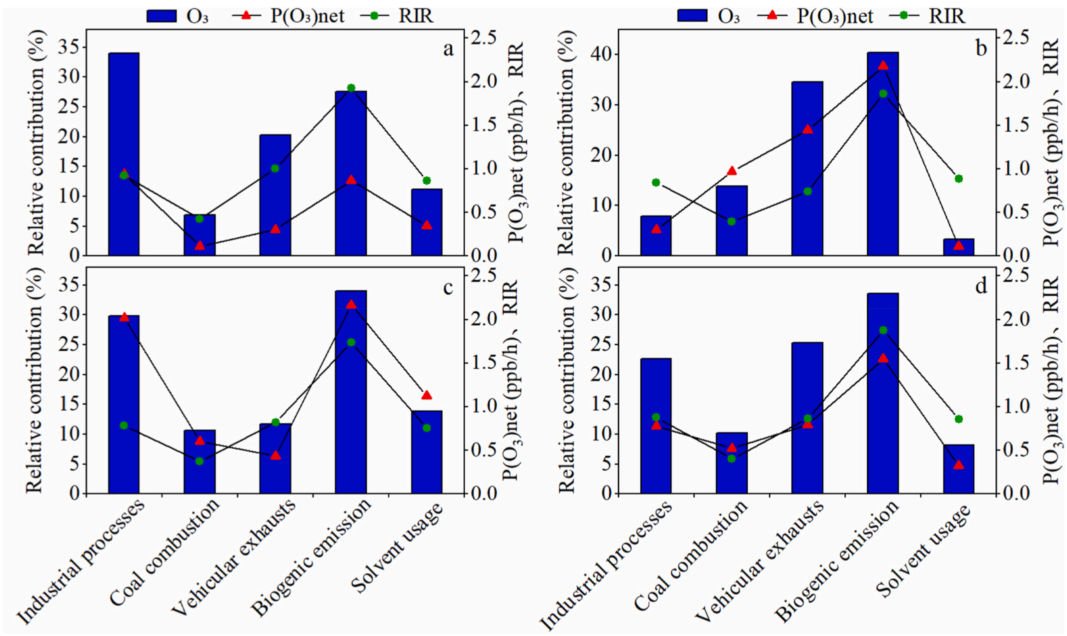

Fig. 6. P(O_3)net values, RIRs of sources, and their contribution to O_3 production during low O_3 episodes (a), moderate O_3 episodes (b), high O_3 episodes (c), and the whole observation period(d).

VOCs source to O_3 formation. The vehicular emissions provided the largest contribution (25.35%) to O_3 production, followed by industrial processes (22.65%), coal combustion (10.21%), and solvent usage (8.19%) during the whole observation period, indicating that VOCs from vehicular emissions and industrial processes exerted a great influence on O_3 formation. The contribution of coal combustion to ambient VOCs was relatively high and served as the third largest source of VOCs (Fig. 3.). However, inversely, its influence on O_3 formation was relatively weak. For different O_3 exposure periods, industrial processes (34.03%) and vehicular emissions (20.27%) were the major sources of O_3 generation during the low O_3 episodes. Vehicular emissions (34.50%) had the largest potential to generate O_3 in the moderate O_3 episodes, while industrial processes (29.81%) were the primary contributor to O_3 production in the high O_3 episodes. Industrial processes and vehicular emissions emitted more active components, such as alkenes and aromatics, which can be consumed during the formation of O_3 through photochemical reactions. In addition, the RIR of VOCs from vehicular emissions and industrial processes were large, but their contributions to O_3 production differed during different O_3 episodes. This phenomenon was mainly due to the fact that the meteorological conditions and

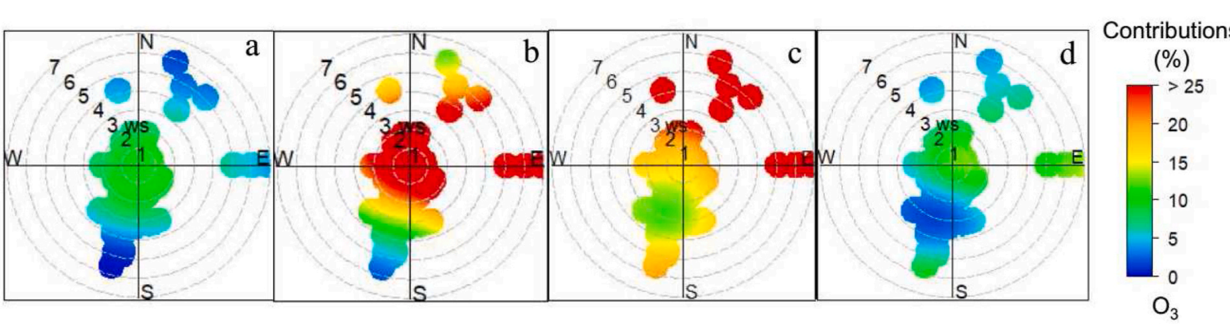

Fig. 7. Windrose showing the contributions of anthropogenic VOCs sources to O_3 production (a: coal combustion; b: vehicular emissions; c: industrial processes; d: solvent usage).

emissions intensities of the sources varied in the different O_3 episodes. Therefore, strictly restricting VOCs emissions from vehicular sources in moderate O_3 episodes and those from industrial processes in high O_3 episodes can reduce the mixing ratios of ambient VOCs, and decrease the formation rates of O_3 during summertime in Taiyuan.

VOCs from vehicular emissions and solvent usage impacted O_3 formation considerably under weak wind speed (<2 m/s, Fig. 7). This is especially true for vehicular emissions, indicating the evidently native characteristic of this source. Industrial processes contributed more than 25% to O_3 formation under strong wind speeds (>4 m/s), suggesting that this VOCs source added to the local O_3 formation via regional transportation (Fig. 7c). The effect of VOCs from coal combustion on O_3 formation was therefore expected to decrease with the energy policy-related readjustments. While the contribution of vehicular emissions to local O_3 production were highlighted. Predictably, vehicular emissions will always be the biggest source of local O_3 formation, given with the future trend of economic development in Taiyuan. Additionally, VOCs from industrial processes are increasing and are likely to be another critical source of VOCs contributing to summertime O_3 production in Taiyuan. The effects of VOCs from local solvent use on O_3 formation was relatively small, and this influence is expected to decrease with improvements in solvent quality in the future. Therefore, vehicular emissions and industrial processes will remain the major influential anthropogenic sources for summertime O_3 production, implying that the key to reducing VOCs and thereby O_3 pollution in Taiyuan involves the synchronous limiting of emissions from vehicles as well as industrial processes while maintaining the coal restriction policies.

All the output results from the zero-dimensional photochemistry model were based on some assumptions and observation data of O_3 and its precursors. However, many observed VOCs can react with atmospheric radicals while being transported from emitters, resulting in uncertainty, especially the high reactivity hydrocarbons. Additionally, due to the neglected oxygenated and halogenated VOCs, the effects of VOCs on O_3 generation will also be overestimated. These uncertainties in observed data and the limited species of VOCs can be propagated through PMF and photochemistry model. Simulation results should reflect the effects of VOCs on summertime O_3 formation but not be deemed as accurately quantitative results in this study. Therefore, future research should take the rapid reactivity of VOCs and more species which contribute to O_3 formation into consideration. More efforts should be made to improve the function of the zero-dimensional photochemistry model to enhance the accuracy and reliability of the simulation results of O_3 production.

3.4. Implications

As the largest anthropogenic contributor of VOCs and O_3 formation, vehicular emissions had the maximum reduction potential in Taiyuan. However, vehicle population was gradually increasing driven by economic development in Taiyuan. Although a series of prevention and control policies, including eliminating the high-emissions and old vehicles, updating emission standards, advocating new energy vehicles and improving the fuel quality, have been gradual implemented, VOCs from vehicular emissions will still be high in the future without constraining the population of vehicles. Population of the high-emission and old vehicles will gradually shrink, and the availability of the corresponding policies will be weakened or even offset over the time. Other policies implemented were conducive to the reduction of VOCs from vehicles, but the reduction potential was limited. More comprehensive policies should be promoted together with these traditional measures in the future. Encouraging public transportation may be an effective strategy to simultaneously reduce the activity of private vehicles, conserve energy and alleviate traffic jams, resulting the pollutants emissions reduction, especially for VOCs. Restricting the vehicles population may be also the most direct and effective policies to control the VOCs and thereby O_3 level. Like many traditional industrial cities in northern China, the emissions from coal combustion and industrial processes have also been impacted by the strategies to reduce dependence on coal and cleaner production implementation in Taiyuan. With the reduced of coal combustion emission as discussed in section 3.2 and the lower chemical reaction capacity of VOCs, effect of coal combustion emissions on O_3 production will be reduced. For industrial processes, the second anthropogenic contributor of O_3 production, its effect on O_3 is expected to decrease with the implementation of VOCs reduction policies, such as industrial restructure, cleaner production, process optimization, and so on. Previous result also indicated that VOCs from vehicle emissions had a higher potential to product O_3 than the O_3 formation potential of VOCs from industrial process emissions (Wu and Xie, 2017). Thus, in addition to the policies already implemented, advocating public transportation and restricting the vehicles population may be the effective policies to tackle the increasing of VOCs and O_3 in the future in Taiyuan, which may be also suitable for many traditional industrial cities in northern China.

4. Conclusions

With the reduction of dependence on coal and the rapid increasing of vehicles population, vehicular emission has become the largest anthropogenic contributor to ambient VOCs and O_3 formation in many traditional industrial cities in northern China. VOCs measurements, the crucial precursors of O_3, were conducted systematically in Taiyuan from May to July to better investigate the major anthropogenic sources of summertime O_3. The mixing ratio of VOCs ranged between 16.97 and 24.79 ppbv, and the highest value of VOCs was measured at the traffic-intensive area in Taiyuan. Vehicular emissions, coal combustion, industrial processes, solvent usage, and biogenic emissions were identified as the major sources of VOCs by the PMF model, accounting for 28.12%, 25.95%, 19.77%, 17.23% and 8.94% of the total ambient VOCs, respectively. Implementing the zero-D photochemistry model with Master Chemical Mechanism (MCMv3.3.1) revealed that VOCs, especially the alkenes group, limited regime of summertime O_3 generation in Taiyuan. Vehicular emissions become the largest anthropogenic contributor to O_3 formation with the contribution of 25.35%, while industrial processes made the most contribution (29.81%) during the high O_3 episodes. Given the restrictions imposed on coal, more diversified control the VOCs from vehicular emissions and industrial processes emissions may be the long-term and effective strategies to alleviate O_3 pollution in Taiyuan.

CRediT authorship contribution statement

Rumei Li: Data curation, Methodology, Writing – original draft. **Yulong Yan:** Methodology, Supervision, Writing – review & editing. **Lin Peng:** Supervision, Project administration. **Fangyuan Wang:** Data curation, Investigation. **Xingcheng Lu:** Validation, Writing – review & editing. **Yuhang Wang:** Validation. **Yang Xu:** Data curation, Investigation. **Cheng Wang:** Data curation, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2021.118759.

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