Atmos. Chem. Phys., 22, 11931–11944, 2022
https://doi.org/10.5194/acp-22-11931-2022

Atmospheric Chemistry and Physics
Open Access

Measurement report: Ambient volatile organic compound (VOC) pollution in urban Beijing: characteristics, sources, and implications for pollution control

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Received: 18 November 2021 – Discussion started: 23 December 2021
Revised: 22 April 2022 – Accepted: 26 April 2022 – Published: 15 September 2022

Abstract. The increasing ozone (O_3) pollution and high fraction of secondary organic aerosols (SOA) in fine particle mass has highlighted the importance of volatile organic compounds (VOCs) in air pollution control. In this work, four intensive field measurements of VOCs during winter of 2018 (from 1 December 2018 to 17 January 2019), spring (15 April to 27 May), summer (17 June to 13 July), and autumn (22 September to 27 November) of 2019 were conducted at an urban site in Beijing to characterize VOC sources and their contributions to air pollution. The total mixing ratio of the 95 quantified VOCs (TVOC) observed in this study ranged from 5.5–118.7 ppbv with the mean value of 34.9 ppbv. Alkanes, OVOCs, and halocarbons were the dominant chemical groups, accounting for 75 %–81 % of the TVOC across the sampling months. The molar ratios of VOCs to NO_x indicated that O_3 formation was limited by VOCs during the whole sampling period. Positive matrix factorization (PMF) analysis showed that diesel vehicle exhaust, gasoline vehicle exhaust, and industrial emissions were the main VOC sources during both the O_3-polluted and $PM_{2.5}$-polluted months. On the basis of O_3 formation impact, VOCs from fuel evaporation and diesel exhaust, particularly toluene, xylenes, *trans*-2-butene, acrolein, methyl methacrylate, vinyl acetate, 1-butene, and 1-hexene, were the main contributors, illustrating the necessity of conducting emission controls on these pollution sources and species to alleviate O_3 pollution. Instead, VOCs from diesel exhaust as well as coal and biomass combustion were found to be the dominant contributors to secondary organic aerosol formation potential (SOAFP), particularly the VOC species of toluene, 1-hexene, xylenes, ethylbenzene, and styrene, and top priority should be given to these for the alleviation of haze pollution. This study provides insights for the government to formulate effective VOC control measures for air pollution in Beijing.

1 Introduction

Ozone (O_3) and fine particulate matter ($PM_{2.5}$) pollution has restricted improvements in air quality in China. Observation data from the Chinese Ministry of Environment and Ecology (MEE) network witnessed an upward trend for O_3 across the country over the period 2013–2019 (Fu et al., 2019; Li et al., 2017, 2020; Shen et al., 2019; Fan et al., 2020). Also, haze pollution occurring at urban sites in recent years has commonly been characterized by enhanced formation of secondary organic aerosol (SOA) in fine particles; e.g., the fraction of SOA in organic aerosols reached 58 % in Xi'an during winter 2018 and 53 % in urban Beijing during winter 2014 (Kuang et al., 2020; Y. J. Li et al., 2017; Sun et al., 2020;

Q. Xu et al., 2019). Volatile organic compounds (VOCs) are key precursors for the formation of O_3 via gas-phase reactions (Odum et al., 1997; Atkinson, 2000; Sato et al., 2010; Huang et al., 2014). In highly polluted urban regions, O_3 formation is generally VOC-limited, and it is suggested that VOC emission control is necessary for effective alleviation of photochemical smog (Liu et al., 2020; Liu and Wang, 2020; Shao et al., 2009; Wang et al., 2020; Xing et al., 2011). In addition, VOCs, including aromatics and biogenic species, have a significant impact on SOA formation, which plays an important role in haze formation (Huang et al., 2014; Tong et al., 2021). VOC emission abatement is therefore imperative for improving air quality in China.

VOCs in ambient air can be emitted by a variety of sources including both anthropogenic and biogenic sources. While biogenic emissions are significantly greater than anthropogenic emissions globally (Doumbia et al., 2021; Sindelarova et al., 2022), anthropogenic emissions play the dominant role in urban and surrounding areas (Warneke et al., 2007; Ahmad et al., 2017; Wu and Xie, 2018). The VOC observations in China showed distinct differences in anthropogenic sources among different regions. For example, solvent use and vehicle exhaust are primary VOC sources in urban Shanghai and urban Guangzhou, while the primary sources of VOCs in Wuhan, Zhengzhou, and Beijing are combustion and vehicle exhaust (Han et al., 2020; Shen et al., 2020; Liu et al., 2020; B. Li et al., 2019). Apart from the diversity of emission sources, different VOC species exhibited different propensities to form O_3 and SOA. Observation-based studies commonly apply the O_3 formation potential (OFP) and SOA formation potential (SOAFP) scales to quantify the relative effects of specific VOCs and sources on O_3 and SOA formation as well as to aid in the development of efficient control strategies (Carter and Atkinson, 1989; Chang and Rudy, 1990; Han et al., 2020; Zhang et al., 2017). Although there have been many studies on ambient VOCs in various locations (e.g., urban, rural, and industrial areas), most of these measurements were confined to short periods (a few days or a certain season), and the understanding of temporal variations in concentrations, sources, and the influence of photochemical reactions of VOCs on an annual scale is still limited. Most of the available reports on VOC analysis based on online analytical techniques include mainly non-methane hydrocarbon compounds, and thus the characteristics of VOCs as well as their relationships with $PM_{2.5}$ and O_3 cannot be fully revealed since OVOCs also actively participate in chemical reactions related to secondary formation (B. Li et al., 2019; Q. Zhao et al., 2020; Yang et al., 2018; Pallavi et al., 2019). Therefore, the long-term and comprehensive monitoring of VOCs is desired.

As the capital and one of the largest megacities in China, Beijing has been suffering from severe O_3 pollution due to rapid economic development and increases in precursor emissions (Y. S. Wang et al., 2014; Wang et al., 2017; Li et al., 2019b; D. Zhao et al., 2020). According to the Report on the State of the Ecology and Environment in Beijing, the average 90th percentile O_3 daily maximum 8 h concentration in Beijing has exceeded the national standards, reaching 193, 192, and 191 $\mu g\,m^{-3}$ in 2017, 2018, and 2019, respectively. In addition, the number of motor vehicles in Beijing reached 6.365 million at of the end of 2019 (http://tjj.beijing.gov.cn/EnglishSite/, last access: 2 October 2021), making Beijing the top city in China in terms of the number of motor vehicles. The existing field measurements in Beijing were mostly conducted before 2016, and observations in most recent years are quite limited (Li et al., 2015, 2019a; Liu et al., 2020; Yang et al., 2018). In this work, ambient air samples were collected at an urban site in Beijing from December 2018 to mid-January 2019, mid-April to late May 2019, mid-June to mid-July 2019, and late September to late November 2019. Several O_3 and $PM_{2.5}$ pollution events were captured during the sampling period. The characteristics and the contribution of specific species and sources of VOCs to O_3 and SOA formation, with a focus on photochemical and haze pollution periods, were analyzed in detail. The results and implications from this study can provide useful guidance for policy makers to alleviate ozone and haze pollution in Beijing.

2 Methodology

2.1 Field measurement

The sampling site is on the roof of a three-floor building on the campus of Tsinghua University (40.00° N, 116.33° E), northwest of a Beijing urban area (Fig. S1 in the Supplement). The altitude of the sampling site is 57 m. This sampling site is surrounded by the school and there are no large emission sources nearby; therefore, it can represent the urban air quality in Beijing. Details of the site description are found in W. Xu et al. (2019).

The air samples were collected using 6 L summa canisters (Entech, USA) with a stable rate of 4.26 $mL\,min^{-1}$. The samples were preprocessed to remove N_2, O_2, CO_2, CO, and H_2O in the samples and to further concentrate the samples in volume by the cryogenic pre-concentrator (model 7100, Entech Instruments Inc., USA). A pressure gauge was used to test if the canister has air leakage before sampling every time, and blanks were prepared using cleaned canisters to fill with high-purity nitrogen. The cryotraps of the precooling system were baked before analyses each day and between every sample. The VOCs in air samples were analyzed by a gas chromatography system that was equipped with a mass spectrometric detector (GC-MS) (Agilent Tech., 7890/5975, USA). The suitability of this system for VOC measurement is well verified, and it has been used in field campaigns (Li et al., 2014; Wu et al., 2016). The oven temperature was programmed at 40° for 3 min initially, then raised to 90 °C at 8° min^{-1}, and later raised to 220 °C at 6° min^{-1}, holding for 9 min. In this work, 95 target VOCs, including 25 alkanes, 8 alkenes, 16 aromatics, 34 halocarbons, and 12 OVOCs, were quantified. It should be noted that VOCs (C2–C3) with a low boiling point (i.e., ethane, ethene, acetylene, and propane) were not detected by the GC-MS system. The standard substance (SPECTRA GASES Inc., USA) mentioned for Photochemical Assessment Monitoring Stations (PAMS) and the US EPA TO-15 standard were used to construct the calibration curves for the target VOCs. Quality assurance and quality control, including the method detection limit (MDL) of each compound, laboratory and field blanks, retention time, accuracy, and duplicate measurements of samples, were performed according to the US EPA Compendium Method TO-15 (US Environmental Protection Agency, 1999). The correlated coefficients of the calibration curves for all the compounds were > 0.95. The relative standard deviation (RSD) for all of compounds of triplicates was 0.5 %–6.0 %. Previous field measurements have reported that the precision of a GC-MS system for hydrocarbons and aldehydes was below 6 % and 15 %, respectively (Li et al., 2014; Wu et al., 2016). In this work, one kind of aldehyde substance, i.e., acrolein, was detected, with R^2 and RSD of 0.99 % and 4.5 %, respectively.

During the sampling periods, the measurements of $PM_{2.5}$, gaseous pollutants (NO_x and O_3), and meteorological variables (such as temperature, relative humidity, wind speed, and wind direction) were conducted simultaneously. SO_2, NO_x, and O_3 were analyzed using a pulsed fluorescence SO_2 analyzer (Thermo Fisher Scientific USA, 43I), chemiluminescence NO–NO_2–NO_x analyzer (Thermo Fisher Scientific USA, 17I), and ultraviolet (UV) photometric O_3 analyzer (Thermo Fisher Scientific USA, 49I), respectively. The mass concentration of $PM_{2.5}$ was measured using an oscillating balance analyzer (TH-2000Z, China) (Y. S. Wang et al., 2014). The quality assurance of SO_2, NO_2, O_3, and $PM_{2.5}$ was conducted based on HJ 630-2011 specifications. Meteorological variables including wind speed (WS), wind direction (WD), relative humidity (RH), air pressure, temperature, and precipitation were measured by an automatic weather monitoring system. The planetary boundary height was obtained from the European Centre for Medium-Range Weather Forecasts (https://www.ecmwf.int/en/forecasts/datasets, last access: 5 November 2021).

2.2 Ozone formation potential (OFP) and secondary formation potential (SOAFP) calculation

The formation potential of O_3 and SOA was used to characterize the relative importance of VOC species and sources in secondary formation, which were estimated using Eqs. (1) and (2):

$$\mathrm{OFP} = \sum\nolimits_i^n \mathrm{MIR}_i \times [\mathrm{VOC(ppb)}]_i, \quad (1)$$

$$\mathrm{SOAFP} = \sum\nolimits_i^n Y_i \times [\mathrm{VOC(ppb)}]_i, \quad (2)$$

where n represents the number of VOCs, $[\mathrm{VOC}]_i$ represents the ith VOC species concentration, MIR_i is the maximum incremental reactivity for the ith VOC species, and Y_i is the SOA yield of VOC_i (McDonald et al., 2018). The MIR for each VOC species was taken from the updated Carter research results (http://www.engr.ucr.edu/~carter/reactdat.htm, last access: 24 February 2021). For species lacking yield curves, the fractional aerosol coefficient (FAC) values proposed by Grosjean and Seinfeld (1989) were used.

2.3 Deweathered model

In this work, the influences of meteorological conditions on O_3 and $PM_{2.5}$ were removed using the random forest (RF) model. The meteorological predictors in the RF model include wind speed (WS), wind direction (WD), air temperature (T), relative humidity (RH), precipitation (Prec), air pressure (P), time predictors (year, day of year – DOY, hour), and planetary boundary layer height (BLH). These meteorological parameters have been reported to be strongly associated with $PM_{2.5}$ and O_3 concentrations in various regions in China (Chen et al., 2020; Feng et al., 2020) and contributed significantly in previous $PM_{2.5}$ and O_3 prediction models (She et al., 2020; Li et al., 2020). The modeling relates the hourly variability of O_3 and $PM_{2.5}$ to that of meteorological variables. The model performance was evaluated through the 10-fold cross-validation (CV) approach, which randomly selects 10 % of the dataset for model testing and trains the model with the remaining data. This process was repeated 10 times, and each record was selected once as testing data. In each round, the training dataset includes ~ 90 % randomly selected data representing different seasons. After the building of the RF model, the deweathered technique was applied to predict the air pollutant level at a specific time point. The differences in original pollutant concentrations and deweathered pollutant concentrations were regarded as the concentrations contributed by meteorology. Statistical indicators including R^2, root mean square error (RMSE), and mean absolute error (MAE) values were regarded as the major criteria to evaluate the modeling performance.

2.4 Positive matrix factorization (PMF)

In this study, the US EPA PMF 5.0 software was used for VOC source apportionment (Abeleira et al., 2017; B. Li et al., 2019; Xue et al., 2017). The detailed description of the PMF model is found elsewhere (Ling et al., 2011; Yuan et al., 2010). PMF uses both concentration and user-provided uncertainty associated with the data to weight individual points. Species with high percentages of missing values (> 40 %) and with signal-to-noise ratio below 2 were excluded. Based on this, 53 VOC species including source tracers (e.g., chloromethane, trichloroethylene, tetrachloroethylene, and MTBE – methyl tert butyl ether) and SO_2 were chosen for the source apportionment analysis. Data values below the MDL were replaced by MDL/2, and the missing data were substituted with median concentrations. If the concentration is less than or equal to the MDL provided, the uncertainty is calculated using the equation $\mathrm{Unc} = 5/6 \times \mathrm{MDL}$; if the concentration is greater than the MDL provided, the uncertainty is calculated as $\mathrm{Unc} = [(\text{error faction} \times \text{mixing ratio})^2 + (\mathrm{MDL})^2]\ 1/2$.

During the PMF analysis, the bootstrap (BS) method, displacement (DISP) analysis, and the combination of the DISP and BS (BS–DISP) were used to evaluate the uncertainty of the base run solution. A total of 100 bootstrap runs were performed, and acceptable results were obtained for all factors (above 90 %). Based on the DISP analysis, the observed drop in the Q value was below 0.1 %, and no factor swap occurred, confirming that the solution was stable. The BS–DISP analysis showed that the observed drop in the Q value was less than 0.5 %, demonstrating that the solution was useful.

3 Results and discussion

3.1 TVOC mixing ratios and chemical composition

The time series of meteorological parameters and concentrations of air pollutants during the measurement period are shown in Fig. 1. The ambient temperature ranged from −13.3 to 38.7°, and the RH varied between 5 % and 99 % across the sampling months. Prevailing winds shifted between southwesterly and northeasterly with WS of 0–6.8 $\mathrm{m\,s^{-1}}$. The mixing ratio of total VOCs (TVOC) ranged from 5.5–118.7 ppbv during the sampling period with relatively higher values during September and November (49.9–51.6 ppbv), while there were relatively lower values (22.2–27.5 ppbv) across the other months. Major VOC compositions were generally consistent during the whole measurement period. Alkanes, OVOCs, and halocarbons were the dominant chemical groups, accounting for 75 %–81 % of the TVOC across the sampling months. In terms of individual species, acetone, dichloromethane, *n*-butane, toluene, methyl tert butyl ether (MTBE), iso-pentane, propylene, *n*-hexane, 1,1-dichloroethane, benzene, and 1-butene made up the largest contribution, accounting for 50.6 % of the TVOC on average during the whole measurement period.

As shown in Fig. 2, the concentrations of TVOC and major VOC groups including alkanes, alkenes, aromatics, halocarbons, and OVOCs observed in this study were apparently lower than those during the sampling months in 2014 and 2016 in urban Beijing (An et al., 2012; Liu et al., 2020; Li et al., 2015), indicating the effectiveness of control measures in most recent years in lowering VOC emission. The composition of major chemical groups also showed remarkable changes, with decreased proportions of alkanes but increased fractions of halocarbons, aromatics, and OVOCs, reflecting the changes in emission source types in most recent years.

During the measurement period, 14 $\mathrm{O_3}$ pollution episodes (days with maximum 8 h average $\mathrm{O_3}$ exceeding 160 $\mathrm{\mu g\,m^{-3}}$) were observed on 17 April, 3–4 May, 16 May, 19–20 June, 24–25 June, 2 July, 5 July, 13 July, 25–26 September, and 28 September 2019. The comparison of meteorological parameters and air pollutants on $\mathrm{O_3}$ pollution and compliance days (days with maximum 8 h average $\mathrm{O_3}$ below 160 $\mathrm{\mu g\,m^{-3}}$) during the 5 $\mathrm{O_3}$-polluted months (i.e., April, May, June, July, and September of 2019) is discussed here. As shown in Fig. 3, the WS on $\mathrm{O_3}$ pollution days ($1.31 \pm 0.90\ \mathrm{m\,s^{-1}}$) was slightly lower than that on $\mathrm{O_3}$ compliance days ($1.47 \pm 1.10\ \mathrm{m\,s^{-1}}$), indicating that precursors were more conductive to being diluted on $\mathrm{O_3}$ compliance days. The variation trend of $\mathrm{O_3}$ and temperature displayed a negative correlation, and the linear correlations between $\mathrm{O_3}$ and temperature on $\mathrm{O_3}$ pollution days ($R^2 = 0.63$) were stronger than that on $\mathrm{O_3}$ compliance days ($R^2 = 0.35$). The mean TVOC concentration on $\mathrm{O_3}$ pollution days (32.3 ppbv) was higher than that on $\mathrm{O_3}$ compliance days (29.6 ppbv), which was mainly attributed to higher concentrations of MTBE, acrolein, and *trans*-2-butene on pollution days. MTBE is widely used as a fuel additive in motor gasoline (Liang et al., 2020), and *trans*-2-butene is the main component of oil and gas evaporation (B. Li et al., 2019). Such a result suggests enhanced contribution of traffic emissions on $\mathrm{O_3}$ pollution days. Also, the concentration of isoprene, which is primarily produced by vegetation through photosynthesis, increased significantly on $\mathrm{O_3}$ pollution days, probably due to stronger plant emissions at elevated temperatures (Guenther et al., 1993, 2012; Stavrakou et al., 2014). The ratio of m/p-xylene to ethylbenzene (X/E) measured can be used as an indicator of the photochemical aging of air masses because of their similar sources in urban environments and differences in atmospheric lifetimes (Carter, 2010; Miller et al., 2012; H. L. Wang et al., 2013). The mean X/E value on $\mathrm{O_3}$ compliance days (1.41) was higher than that on $\mathrm{O_3}$ pollution days (1.17), indicating enhanced secondary transformation of VOCs on $\mathrm{O_3}$ pollution days.

The daily $\mathrm{PM_{2.5}}$ concentrations ranged from 9–260 $\mathrm{\mu g\,m^{-3}}$ with the mean value of 88.5 $\mathrm{\mu g\,m^{-3}}$ during the measurement period. 15 $\mathrm{PM_{2.5}}$ pollution days (daily average $\mathrm{PM_{2.5}}$ exceeding 75 $\mathrm{\mu g\,m^{-3}}$) were observed on 3 January, 12–13 January, 22–23 April, 29 April, 12 May, 15 May, 19 October, 21–23 November 2019, 1–2 December, and 5 December 2018. During the six $\mathrm{PM_{2.5}}$-polluted months (i.e., December 2018, January, April, May, October, and November 2019), the WS on $\mathrm{PM_{2.5}}$ pollution days ($1.05 \pm 1.06\ \mathrm{m\,s^{-1}}$) was lower than that on $\mathrm{PM_{2.5}}$ compliance days ($1.43 \pm 1.06\ \mathrm{m\,s^{-1}}$), indicating the weaker ability of winds to dilute and diffuse precursors on $\mathrm{PM_{2.5}}$ pollution days. The mean X/E value on $\mathrm{PM_{2.5}}$ compliance days (1.47) was slightly higher than that on $\mathrm{PM_{2.5}}$ pollution days (1.44), indicating enhanced secondary transformation of VOCs on $\mathrm{PM_{2.5}}$ pollution days.

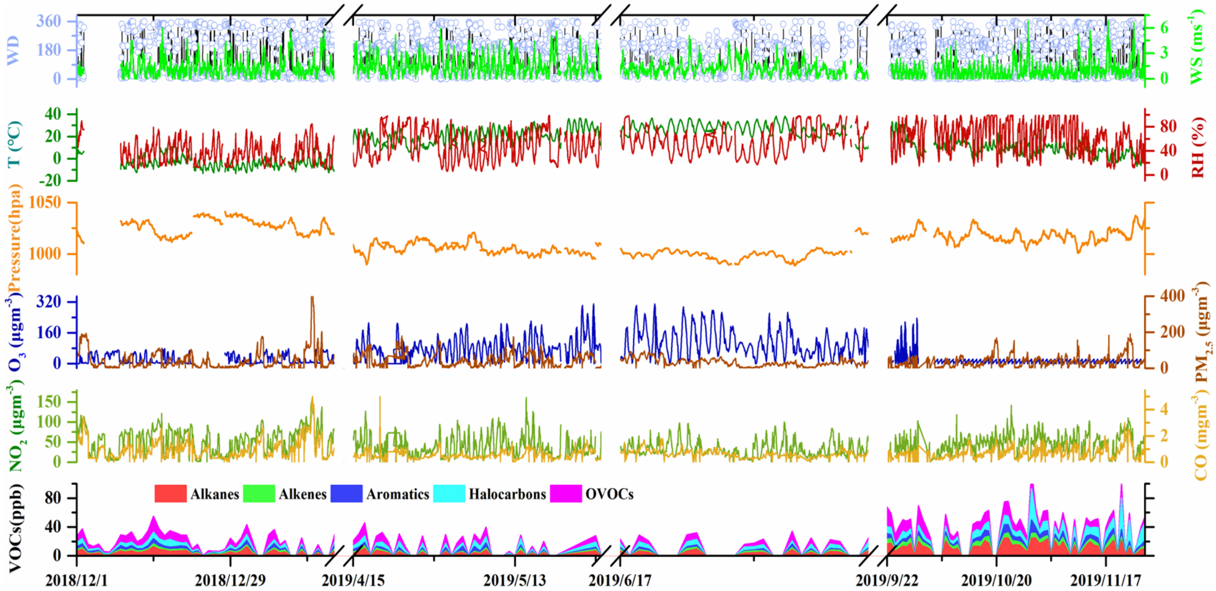

Figure 1. Time series of meteorological parameters and levels of air pollutants during the sampling period.

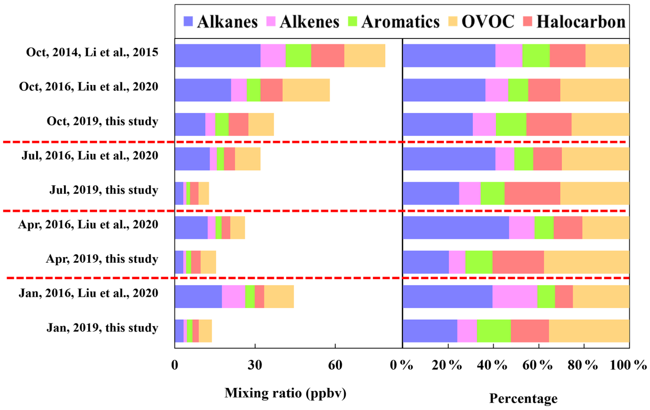

Figure 2. Comparison of the concentration and composition of major chemical groups observed in 2019 (this study), 2016 (Liu et al., 2020), and 2014 (Li et al., 2015).

3.2 The role of VOCs in secondary pollution

3.2.1 Estimating O_3 and $PM_{2.5}$ levels contributed by emissions

O_3 and secondary aerosols are primarily formed via photochemical reactions in the atmosphere, concentrations of which could be largely influenced by meteorological conditions (Chen et al., 2020; Feng et al., 2020; Zhai et al., 2019). In this work, the respective contributions of meteorology and emissions to $PM_{2.5}$ and O_3 variations were determined using the RF model as described in Sect. 2.3. The coefficients of determination (R^2) for the RF model in predicting $PM_{2.5}$ and O_3 are 0.85 and 0.91, respectively (shown in Fig. S2). The respective contributions of anthropogenic emissions and meteorology to O_3 and $PM_{2.5}$ during each period is shown in Fig. 4. During the O_3-polluted months, the meteorologically driven O_3 level on O_3 pollution days ($72.5\,\mu g\,m^{-3}$) was significantly higher than that on O_3 compliance days ($35.3\,\mu g\,m^{-3}$). After removing the meteorological contribution, the residual emission-driven O_3 level on O_3 pollution ($45.3\,\mu g\,m^{-3}$) and compliance days ($44.9\,\mu g\,m^{-3}$) of the O_3-polluted months was almost identical and was significantly higher than that during the non-O_3-polluted months ($23.8\,\mu g\,m^{-3}$). The emission-driven $PM_{2.5}$ level was in the order of: $PM_{2.5}$ pollution days of the $PM_{2.5}$-polluted months ($55\,\mu g\,m^{-3}$) > $PM_{2.5}$ compliance days of the $PM_{2.5}$-polluted months ($44\,\mu g\,m^{-3}$) > non-$PM_{2.5}$-polluted months ($29\,\mu g\,m^{-3}$). These results suggest that apart from meteorological factors, emissions also play a role in deteriorating $PM_{2.5}$ and O_3 pollution, and reducing anthropogenic emissions is essential for improving air quality.

The VOCs/NO_x ratio has been widely used to distinguish whether O_3 formation is VOC-limited or NO_x-limited (B. Li et al., 2019). Generally, a VOC-sensitive regime occurs when VOCs/NO_x ratios are below 10, while an NO_x-sensitive regime occurs when VOCs/NO_x ratios are higher than 20 (Hanna et al., 1996; Sillman, 1999). In this study, the values of VOCs/NO_x (ppbv ppbv^{-1}) were all below 3 during both the O_3-polluted and non-O_3-polluted months (Fig. S3), suggesting that O_3 formation was sensitive to VOCs, and thus the reductions of the emissions of VOCs will be beneficial for O_3 alleviation.

3.2.2 Contribution of VOCs to OFP and SOAFP

As discussed in Sect. 3.2.1, O_3 formation was generally VOC-sensitive during the measurement period. Quantifying

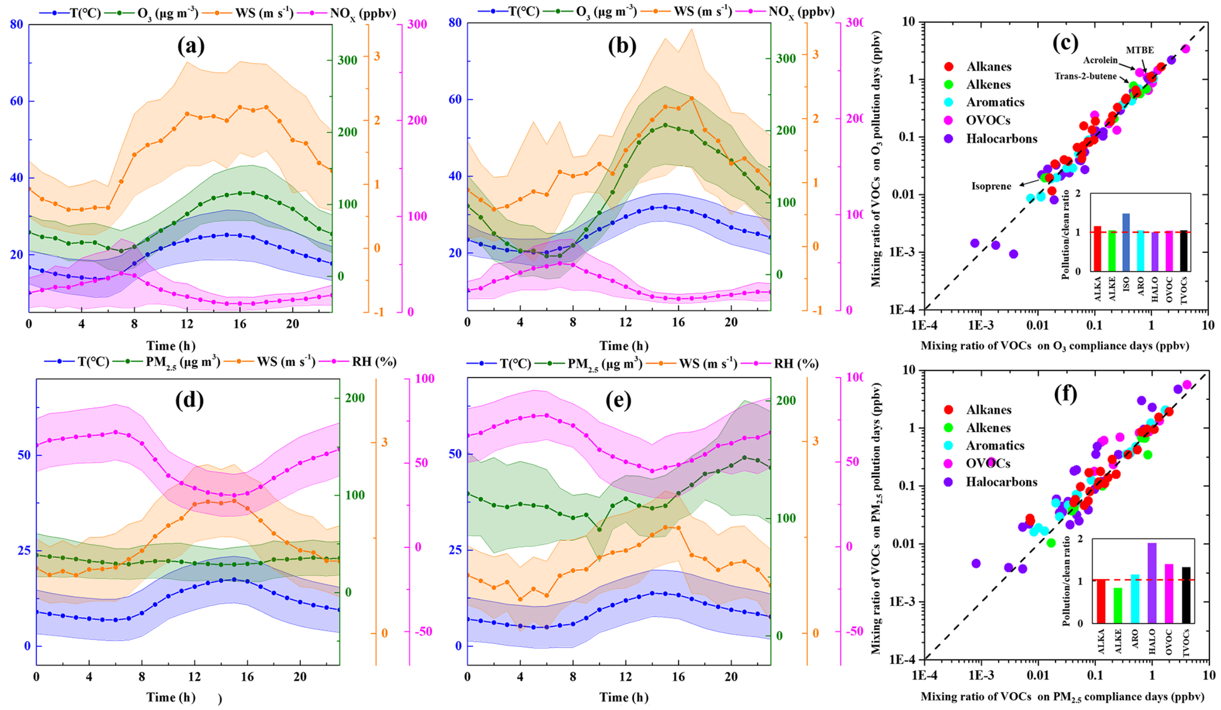

Figure 3. The averaged levels of temperature (T), wind speed (WS), and O_3 and NO_x concentrations on **(a)** O_3 compliance days during the O_3-polluted months, **(b)** O_3 pollution days during the O_3-polluted months, and **(c)** differences in VOC mixing ratios between O_3 compliance and pollution days. The averaged levels of temperature (T), wind speed (WS), relative humidity (RH), and $PM_{2.5}$ concentrations on **(d)** $PM_{2.5}$ compliance days during the $PM_{2.5}$-polluted months, **(e)** $PM_{2.5}$ pollution days during the $PM_{2.5}$-polluted months, and **(f)** differences in VOC mixing ratios between $PM_{2.5}$ compliance and pollution days.

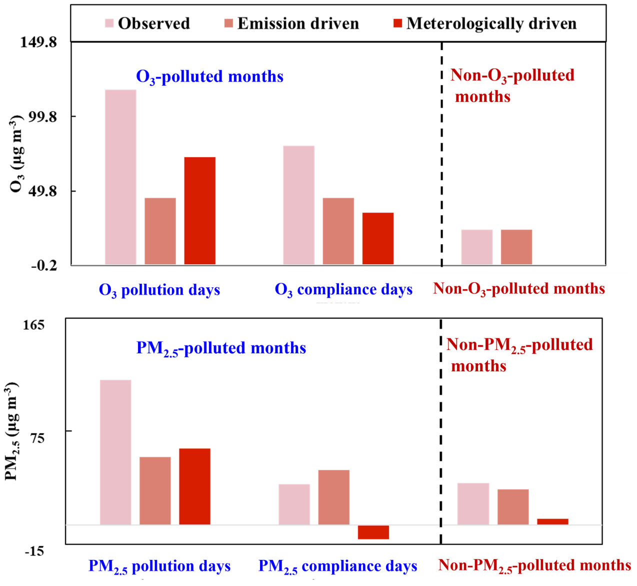

Figure 4. Statistic decomposition of meteorological and emission contribution to O_3 and $PM_{2.5}$ levels during different periods.

the contribution of speciated VOC species to O_3 is helpful for developing effective VOC control measures and alleviating O_3 pollution. The averaged OFPs on O_3 pollution days of the O_3-polluted months, O_3 compliance days of the O_3-polluted months, and during the non-O_3-polluted months were 224.9, 201.4, and 187.5 $\mu g\,m^{-3}$, respectively (Fig. 5). According to our observations, the higher OFP on O_3 pollution days than on O_3 compliance days during the O_3-polluted months was mainly attributed to higher levels of *trans*-2-butene, *o*-xylene, and acrolein O_3 on pollution days, in line with Fig. 3. Alkenes, aromatics, and OVOCs were the three biggest contributors to O_3 formation, accounting for 85.1 %, 85.7 %, and 81.6 % of the total OFP on O_3 pollution days of the O_3-polluted months, O_3 compliance days of the O_3-polluted months, and during the non-O_3-polluted months, respectively. In terms of the individual species, the top 10 highest contributors during the O_3-polluted months were toluene (6.4 % and 7.5 % on O_3 pollution and compliance days, respectively), *trans*-2-butene (9.6 % and 7.5 %), acrolein (10.8 % and 5.7 %), *m*/*p*-xylene (6.1 % and 6.9 %), *o*-xylene (6.6 % and 5.8 %), 1-butene (5.2 % and 7.1 %), 1-hexene (4.4 % and 5.4 %), vinyl acetate (4.2 % and 5.7 %), methyl methacrylate (5.5 % and 4.8 %), and 1-pentene (4.5 % and 4.4 %). During the non-O_3-polluted months, the overall OFP was mainly contributed by toluene (10.8 %), *trans*-

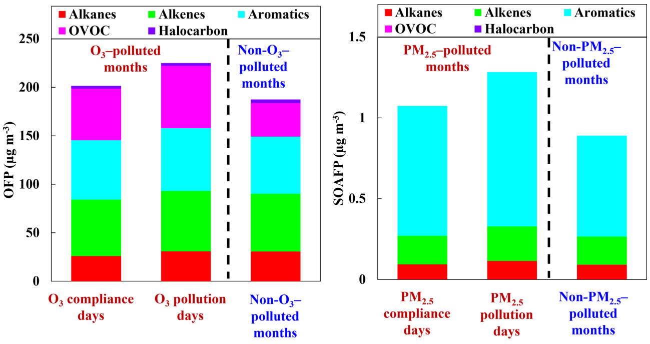

Figure 5. OFP and SOAFP by chemical groups during different periods.

2-butene (10.5 %), 1-butene (7.3 %), *m*/*p*-xylene (6.5 %), 1-pentene (5.7 %), 1-hexene (5.0 %), methyl methacrylate (4.9 %), *o*-xylene (4.9 %), vinyl acetate (3.8 %), and isopentane (2.3 %).

As shown in Fig. S3, the ratio of VOCs/NO_x was generally below 3 during the sampling period, indicating high NO_x conditions. Based on the estimated yields of the VOCs shown in Table S2, the SOAFPs were calculated and compared in Fig. 5. The mean SOAFPs on $PM_{2.5}$ pollution days of the $PM_{2.5}$-polluted months, $PM_{2.5}$ compliance days of the $PM_{2.5}$-polluted months, and during the non-$PM_{2.5}$-polluted months were 1.28, 1.07, and 0.89 µg m^{-3}. During the 6 $PM_{2.5}$-polluted months, the higher SOAFP on $PM_{2.5}$ pollution days than on $PM_{2.5}$ compliance days was mainly attributed to higher levels of 1,2,4-trimethylbenzene, *n*-undecane, *n*-nonane, 1,4-diethylbenzene, and 1,3-diethylbenzene on $PM_{2.5}$ pollution days. Aromatics have the largest SOAFP, accounting for 74 % and 75 % of the total SOAFP for $PM_{2.5}$ pollution and compliance days of the $PM_{2.5}$-polluted months and 70 % of the total SOAFP during the non-$PM_{2.5}$-polluted months, respectively. The 10 species responsible for most of the SOAFP were toluene (41 % and 40 % on $PM_{2.5}$ pollution and compliance days of the $PM_{2.5}$-polluted months,= and 33 % during the non-$PM_{2.5}$-polluted months), 1-hexene (13.0 %, 12.5 %, and 15.2 %), xylenes (11.6 %, 14.1 %, and 14.8 %), ethylbenzene (4.9 %, 5.3 %, and 6.0 %), styrene (4.5 %, 5.6 %, and 5.6 %), 1-pentene (3.3 %, 3.4 %, and 4.3 %), methyl cyclopentane (2.1 %, 2.7 %, and 3.6 %), 1,2,3-trimethylbenzene (2.8 %, 2.4 %, and 2.8 %), *m*-ethyl toluene (1.7 %, 1.4 %, and 1.7 %), and *p*-ethyl toluene (1.7 %, 1.4 %, and 1.7 %).

3.3 Source apportionment of VOCs

3.3.1 Indication from tracers

The great changes in the mixing ratios of different species are mainly affected by photochemical processing, emission inputs, and ratios of VOC species having similar atmospheric lifetimes can reflect the source features (B. Li et al., 2019; Raysoni et al., 2017; Song et al., 2021). The ratio of *i*-pentane to *n*-pentane is widely used to examine the impact of vehicle emissions, fuel evaporation, and combustion emissions within the *i*/*n*-pentane ratios of ranging 2.2–3.8, 1.8–4.6, and 0.56–0.80, respectively (McGaughey et al., 2004; Jobson et al., 2004; Russo et al., 2010; M. Wang et al., 2013; Yan et al., 2017). As shown in Fig. 6, the *i*/*n*-pentane ratios during the $PM_{2.5}$-polluted months were mostly within the range of 0.3–2.0, suggesting the pentanes were from mixed sources of coal combustion and fuel evaporation. During the non-$PM_{2.5}$-polluted months, the *i*/*n*-pentane ratios were distributed in the range of 1.3–3.4, indicating strong impacts from vehicle exhaust and fuel evaporation. During the O_3-polluted months, most of the *i*/*n*-pentane ratios (1.5–2.5) were distributed within the reference range of vehicle exhaust and fuel evaporation, whereas most of the *i*/*n*-pentane ratios during the non-O_3-polluted months ranged 1.7–2.1, suggesting the significant impact of fuel evaporation.

The toluene / benzene (T/B) ratio is a widely used indicator for sources of aromatics. In areas heavily impacted by vehicle emissions, the T/B ratio lies in the range of 0.9–2.2 (Qiao et al., 2012; Dai et al., 2013; J. Wang et al., 2013; Yao et al., 2013; Zhang et al., 2013; Yao et al., 2015; Mo et al., 2016; Deng et al., 2018). Higher T/B ratios were reported for solvent use (greater than 8.8) (Yuan et al., 2010; H. Wang et al., 2014; Zheng et al., 2013) and industrial processes (1.4–5.8) (Mo et al., 2015; Shi et al., 2015). In burning source emission studies, the T/B ratio was below 0.6 in different combustion process and raw materials (Tsai et al., 2003; Akagi et al., 2011; Mo et al., 2016). Most of the T/B ratios during the $PM_{2.5}$-polluted and non-$PM_{2.5}$-polluted months were within the range of 1.1–1.8 and 0.8–2.2, whereas the T/B ratios were mostly distributed within the range of 0.8–2.2 and 0.9–1.9 during the O_3-polluted and non-O_3-polluted months, respectively, suggesting the significant impact of vehicle and industrial emissions.

3.3.2 PMF

The factor profiles given by PMF and the contribution of each source to ambient VOCs during each period are presented in Figs. 7 and 8, respectively. Six emission sources were identified: coal and biomass burning, solvent use, industrial sources, oil gas evaporation, gasoline vehicle emission, and diesel vehicle emission based on the corresponding markers for each source category. In general, diesel vehicle exhaust, gasoline vehicle exhaust, and industrial emissions were the main VOC sources during both the O_3-polluted and $PM_{2.5}$-polluted months, with total contributions of 62 % and 62 % on O_3 pollution and compliance days of the O_3-polluted months, as well as 66 % and 59 % on $PM_{2.5}$ pollution and compliance days of the $PM_{2.5}$-polluted months, respectively. The O_3-polluted months exhibited higher proportions of diesel (24 % on O_3 compliance days and 27 % on O_3 pollution days) and gasoline vehicle emission (17 % on O_3

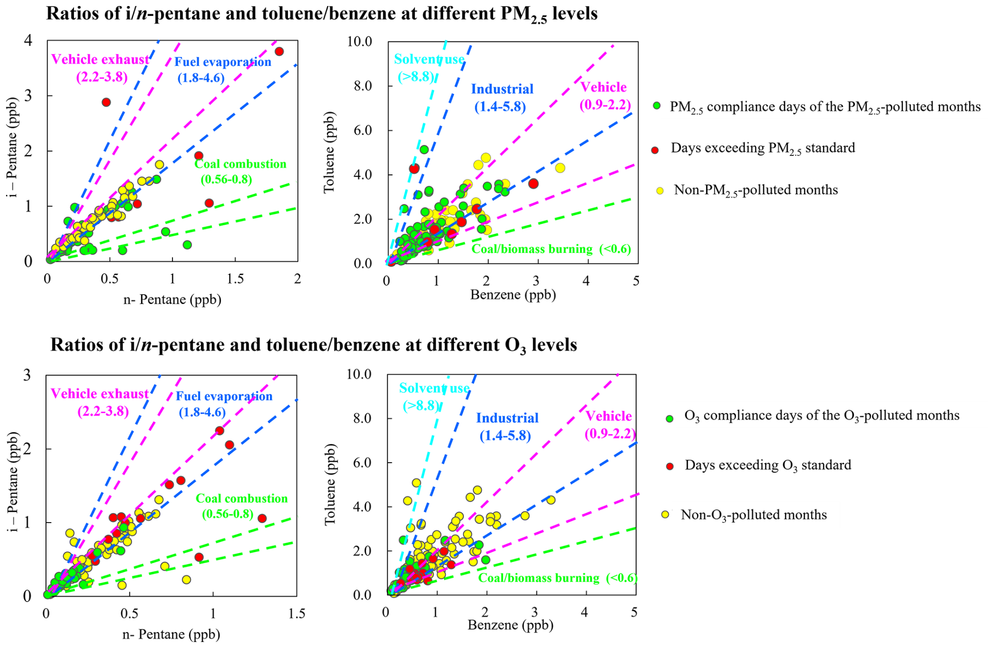

Figure 6. Ratios of i- to n-pentane and toluene to benzene at different $PM_{2.5}$ and O_3 levels.

compliance days and 16 % on O_3 pollution days) compared with the non-O_3-polluted months (8 % and 13 %, respectively). During the O_3-polluted months, the contributions of industrial emissions (22 %) and fuel evaporation (18 %) on O_3 pollution days were much higher than those on O_3 compliance days (18 % and 13 %, respectively). Figure 9 presents the relative contributions of individual VOC sources from PMF to OFP. On the basis of O_3 formation impact, diesel and gasoline vehicle exhaust were major contributors. During the O_3-polluted months, vehicle emissions and fuel evaporation showed higher OFP values on O_3 pollution days (93.9 and 35.5 $\mu g\,m^{-3}$) compared with those on O_3 compliance days (88.0 and 25.8 $\mu g\,m^{-3}$, respectively). Although industrial emissions act as an important source for VOC concentrations on O_3 pollution days (shown in Fig. 8), the potential to form O_3 is limited, accounting for 11 % of the total OFP. As illustrated in Fig. 7, the industrial source was distinguished by high compositions of alkanes but relatively lower compositions of alkenes and aromatics, resulting in low O_3 formation potentials. Such results suggested that the fuel use and diesel vehicle exhaust should be preferentially controlled for O_3 mitigation.

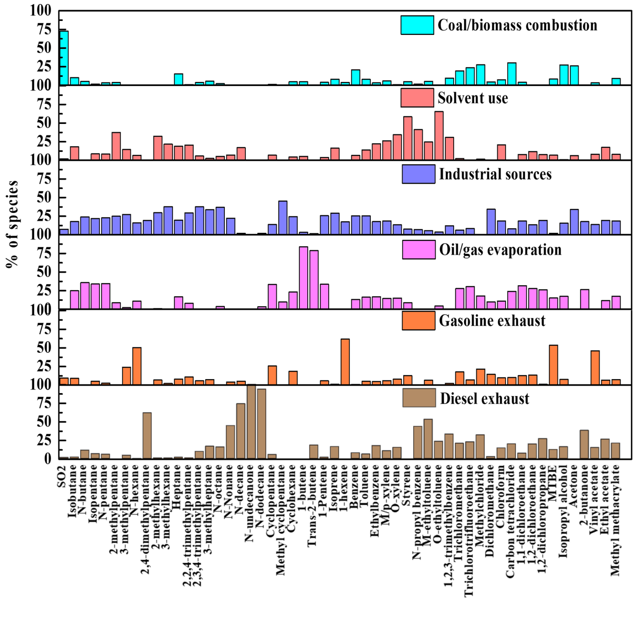

Figure 7. Source profiles of VOCs identified using the PMF model and the relative contributions of the individual VOC species.

The $PM_{2.5}$-polluted months showed higher proportions of industrial (29 % on both $PM_{2.5}$ compliance and $PM_{2.5}$ pollution days) as well as coal and biomass combustion emissions (16 % on $PM_{2.5}$ compliance days and 18 % on $PM_{2.5}$ pollution days) compared with the non-$PM_{2.5}$-polluted months (17 % and 10 %, respectively). The $PM_{2.5}$ pollution days were dominated by industrial emission (29 %), diesel vehicle exhaust (24 %), and combustion sources (18 %). During the $PM_{2.5}$-polluted months, the contribution of diesel vehicle exhaust on $PM_{2.5}$ pollution days (24 %) was higher than that on $PM_{2.5}$ compliance days (16 %). On the basis of $PM_{2.5}$ formation impact, diesel vehicle exhaust and combustion were two major contributors on $PM_{2.5}$ pollution days (shown in Fig. 9), and these two sources showed obvious higher SOAFP on $PM_{2.5}$ pollution days (0.30 and 0.32 $\mu g\,m^{-3}$, respectively) compared with those on $PM_{2.5}$ compliance days

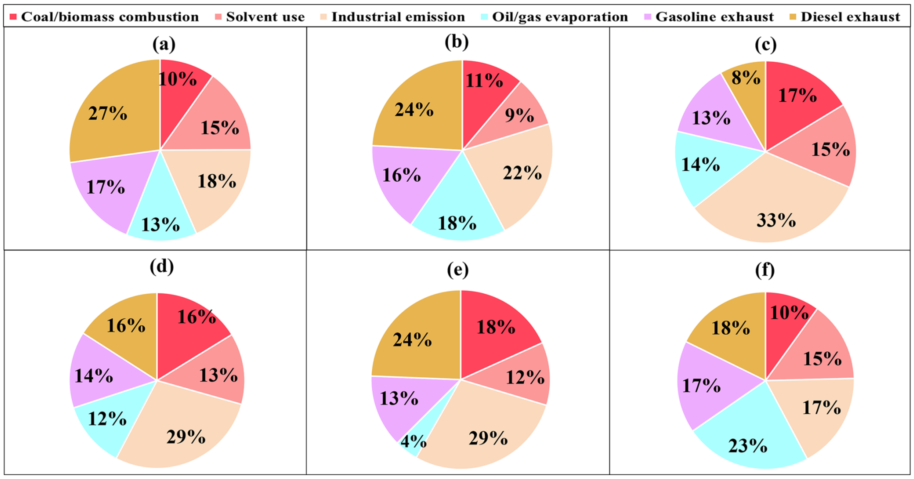

Figure 8. Contributions of each source to VOCs on **(a)** O_3 compliance days during the O_3-polluted months, **(b)** O_3 pollution days during the O_3-polluted months, and during **(c)** the non-O_3-polluted months. Contributions of each source to VOCs on **(d)** $PM_{2.5}$ compliance days during the $PM_{2.5}$-polluted months, **(e)** $PM_{2.5}$ pollution days during the $PM_{2.5}$-polluted months, and **(f)** during the non-$PM_{2.5}$-polluted months.

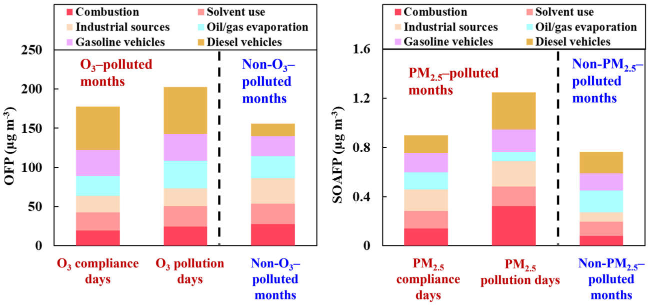

Figure 9. Contributions of each source to OFP and SOAFP during different periods.

of the $PM_{2.5}$-polluted months (0.15 and 0.14 μg m^{-3}, respectively). Although industrial emissions act as an important source for VOC concentrations on $PM_{2.5}$pollution days, the potential to form $PM_{2.5}$ is limited, accounting for 16 % of the total SOAFP. The above results suggested that diesel vehicle exhaust and combustion should be preferentially controlled to alleviate $PM_{2.5}$ pollution.

Based on the mass concentrations of individual species in each source, the following were the dominant species contributing to photochemical O_3 formation: *m*/*p*-xylene, *o*-xylene, methyl methacrylate, vinyl acetate, 1-hexene, and acrolein in gasoline and diesel vehicular emissions; toluene, *trans*-2-butene, and 1-pentene in fuel evaporation and diesel vehicular emissions; and acrolein in solvent, gasoline vehicular, and diesel vehicular emissions (Fig. 10). The following were the dominant contributors to SOA formation during the $PM_{2.5}$ pollution periods (Fig. 10): toluene, *m*/*p*-xylene, *o*-xylene, styrene, ethylbenzene, 1-pentene, and 1,2,3-trimethylbenzene from combustion and diesel vehicular emissions; 1-hexene from diesel vehicular emissions; and methyl cyclopentane from combustion, industrial, and diesel vehicular emissions.

3.4 Limitation

This study analyzed the VOC sources and their contributions to O_3 and SOA formation across different seasons. It should be pointed out that the sampling campaign for VOC measurement was not conducted continuously during December 2018 and November 2019. For instance, the air samples were not collected in August and February–March 2019, during which pollution events of O_3 and $PM_{2.5}$ occurred, respectively. The variations, sources, and secondary transformation potentials of VOCs, particularly for O_3 and $PM_{2.5}$ pollution periods, cannot be fully depicted. Despite the uncertainties that remain, the results obtained in this study provide useful information for VOC emission control strategies and assist in overcoming air pollution issues in Beijing.

4 Conclusions

In this work, a field sampling campaign of VOCs was conducted in urban Beijing from December 2018 to November 2019. The VOC concentrations ranged from 5.5 to 118.7 ppbv with a mean value of 34.9 ppbv. Alkanes, OVOCs, and halocarbons were the dominant chemical groups, accounting for 75 %–81 % of the TVOC across the sampling months. By excluding the meteorological impact, the emission-driven O_3 levels during the O_3-polluted months were higher than during the non-O_3-polluted months, and a similar pattern was found for $PM_{2.5}$. The molar ratio of VOCs to NO_x indicated that O_3 formation was limited by VOCs during both the O_3-polluted non-O_3-polluted months, and thus reducing VOC emissions is essential for allevia-

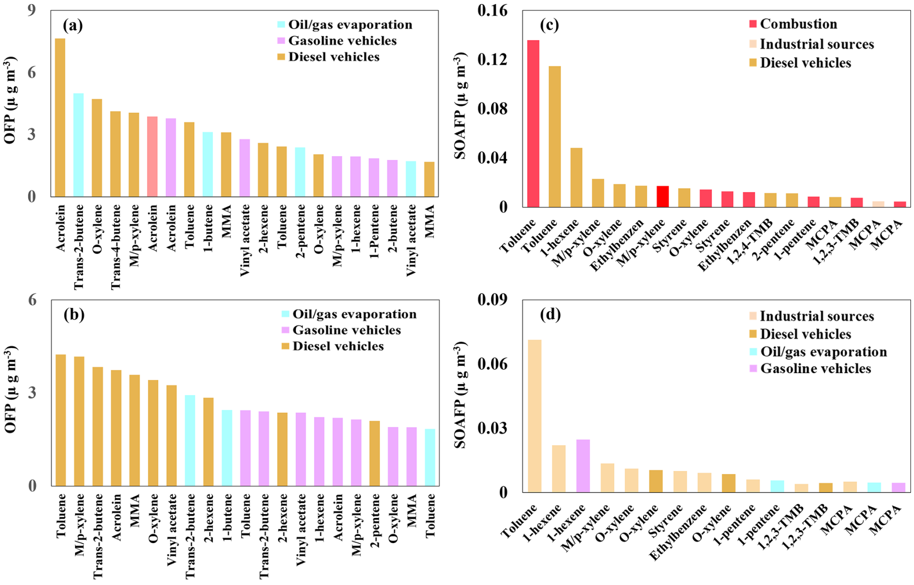

Figure 10. OFP values of the dominant VOC species in the different source categories for the O_3 pollution **(a)** and compliance **(b)** days of the O_3-polluted months. SOAFP values for the $PM_{2.5}$ pollution **(c)** and compliance **(d)** days of the $PM_{2.5}$-polluted months.

tion of O_3 pollution. The contributions of coal and biomass combustion, solvent use, industrial sources, oil and gas evaporation, gasoline exhaust, and diesel exhaust were identified based on PMF analysis. Considering both the concentration and maximum incremental reactivity of individual VOC species for each source, fuel use and diesel exhaust sources were identified as the main contributors of O_3 formation during the O_3-polluted months, particularly the VOC species of toluene, xylenes, *trans*-2-butene, acrolein, methyl methacrylate, vinyl acetate, 1-butene, and 1-hexene, illustrating the necessity of conducting emission controls on these pollution sources and species to alleviate O_3 pollution. VOCs from diesel vehicles and combustion were found to be the dominant contributors for SOAFP, particularly the VOC species of toluene, 1-hexene, xylenes, ethylbenzene, and styrene, and top priority should be given to these for the alleviation of haze pollution.

Data availability. Meteorological data and concentrations of air pollutants including $PM_{2.5}$, O_3, and NO_x are available from the authors upon request. The daily mixing ratio of individual VOC species can be accessed through https://doi.org/10.5281/zenodo.6888723 (Cui et al., 2022).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-22-11931-2022-supplement.

Author contributions. DW designed the study and performed the VOC measurements. QX and RH assisted in air sampling and data collection. LC performed the data analysis and wrote the paper with contributions from all co-authors. SW and JH reviewed the paper and provided comments for improving the paper.

Competing interests. The contact author has declared that none of the authors has any competing interests.

Financial support. This work was supported by the National Natural Science Foundation of China (grant no. 92044302) and the Beijing Municipal Science and Technology Project (grant nos. Z211100004321006 and Z191100009119001).

Review statement. This paper was edited by Eleanor Browne and reviewed by two anonymous referees.

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