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

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Abstract. The increasing ozone (O3) 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 NOx indicated that O3 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 O3-polluted and PM2.5-polluted months. On the basis of O3 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 O3 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 (O3) and fine particulate matter (PM2.5) 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 O3 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 O₃ via gas-phase reactions (Odum et al., 1997; Atkinson, 2000; Sato et al., 2010; Huang et al., 2014). In highly polluted urban regions, O₃ 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; Sin-delarova 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., 2019; 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 O₃ and SOA. Observation-based studies commonly apply the O₃ formation potential (OFP) and SOA formation potential (SOAFP) scales to quantify the relative effects of specific VOCs and sources on O₃ 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 PM₂.₅ and O₃ 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 O₃ 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 O₃ daily maximum 8h concentration in Beijing has exceeded the national standards, reaching 193, 192, and 191 µg m⁻³ in 2017, 2018, and 2019, respectively. In addition, the number of motor vehicles in Beijing reached 6.365 million at 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 O₃ and PM₂.₅ pollution events were captured during the sampling period. The characteristics and the contribution of specific species and sources of VOCs to O₃ 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 6L summa canisters (Entech, USA) with a stable rate of 4.26 mL min⁻¹. The samples were preprocessed to remove N₂, O₂, CO₂, CO, and H₂O 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 cryotrap 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$_3$ 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$_x$, 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):

\[
\text{OFP} = \sum_i^n \text{MIR}_i \times [\text{VOC(ppb)}]_i, \tag{1}
\]

\[
\text{SOAFP} = \sum_i^n Y_i \times [\text{VOC(ppb)}]_i, \tag{2}
\]

where $n$ represents the number of VOCs, $[\text{VOC}]_i$ represents the $i$th VOC species concentration, MIR$_i$ is the maximum incremental reactivity for the $i$th 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 (https://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 as Unc = [(error fraction x mixing ratio)² + (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 °C, 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 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 O₃ pollution episodes (days with maximum 8-h average O₃ exceeding 160 µg 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 O₃ pollution and compliance days (days with maximum 8-h average O₃ below 160 µg m⁻³) during the 5 O₃-polluted months (i.e., April, May, June, July, and September of 2019) is discussed here. As shown in Fig. 3, the WS on O₃ pollution days (1.31 ± 0.90 m s⁻¹) was slightly lower than that on O₃ compliance days (1.47 ± 1.10 m s⁻¹), indicating that precursors were more conducive to being diluted on O₃ compliance days. The variation trend of O₃ and temperature displayed a negative correlation, and the linear correlations between O₃ and temperature on O₃ pollution days ($R^2 = 0.63$) were stronger than that on O₃ compliance days ($R^2 = 0.35$). The mean TVOC concentration on O₃ pollution days (32.3 ppbv) was higher than that on O₃ 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 O₃ pollution days. Also, the concentration of isoprene, which is primarily produced by vegetation through photosynthesis, increased significantly on O₃ 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 O₃ compliance days (1.41) was higher than that on O₃ pollution days (1.17), indicating enhanced secondary transformation of VOCs on O₃ pollution days.

The daily PM$_{2.5}$ concentrations ranged from 9–260 µg m⁻³ with the mean value of 88.5 µg m⁻³ during the measurement period. 15 PM$_{2.5}$ pollution days (daily average PM$_{2.5}$ exceeding 75 µg 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 PM$_{2.5}$-polluted months (i.e., December 2018, January, April, May, October, and November 2019), the WS on PM$_{2.5}$ pollution days (1.05 ± 0.16 m s⁻¹) was lower than that on PM$_{2.5}$ compliance days (1.43 ± 0.16 m s⁻¹), indicating the weaker ability of winds to dilute and diffuse precursors on PM$_{2.5}$ pollution days. The mean X/E value on PM$_{2.5}$ compliance days (1.47) was slightly higher than that on PM$_{2.5}$ pollution days (1.44), indicating enhanced secondary transformation of VOCs on PM$_{2.5}$ pollution days.
3.2 The role of VOCs in secondary pollution

3.2.1 Estimating O\textsubscript{3} and PM\textsubscript{2.5} levels contributed by emissions

O\textsubscript{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\textsubscript{2.5} and O\textsubscript{3} variations were determined using the RF model as described in Sect. 2.3. The coefficients of determination (R\textsuperscript{2}) for the RF model in predicting PM\textsubscript{2.5} and O\textsubscript{3} are 0.85 and 0.91, respectively (shown in Fig. S2). The respective contributions of anthropogenic emissions and meteorology to O\textsubscript{3} and PM\textsubscript{2.5} during each period is shown in Fig. 4. During the O\textsubscript{3}-polluted months, the meteorologically driven O\textsubscript{3} level on O\textsubscript{3} pollution days (72.5 µg m\textsuperscript{-3}) was significantly higher than that on O\textsubscript{3} compliance days (35.3 µg m\textsuperscript{-3}). After removing the meteorological contribution, the residual emission-driven O\textsubscript{3} level on O\textsubscript{3} pollution days (45.3 µg m\textsuperscript{-3}) and compliance days (44.9 µg m\textsuperscript{-3}) of the O\textsubscript{3}-polluted months was almost identical and was significantly higher than that during the non-O\textsubscript{3}-polluted months (23.8 µg m\textsuperscript{-3}). The emission-driven PM\textsubscript{2.5} level was in the order of: PM\textsubscript{2.5} pollution days of the PM\textsubscript{2.5}-polluted months (55 µg m\textsuperscript{-3}) > PM\textsubscript{2.5} compliance days of the PM\textsubscript{2.5}-polluted months (44 µg m\textsuperscript{-3}) > non-PM\textsubscript{2.5}-polluted months (29 µg m\textsuperscript{-3}). These results suggest that apart from meteorological factors, emissions also play a role in deteriorating PM\textsubscript{2.5} and O\textsubscript{3} pollution, and reducing anthropogenic emissions is essential for improving air quality.

The VOCs/NO\textsubscript{x} ratio has been widely used to distinguish whether O\textsubscript{3} formation is VOC-limited or NO\textsubscript{x}-limited (B. Li et al., 2019). Generally, a VOC-sensitive regime occurs when VOCs/NO\textsubscript{x} ratios are below 10, while an NO\textsubscript{x}-sensitive regime occurs when VOCs/NO\textsubscript{x} ratios are higher than 20 (Hanna et al., 1996; Sillman, 1999). In this study, the values of VOCs/NO\textsubscript{x} (ppbv/ppbv\textsuperscript{-1}) were all below 3 during both the O\textsubscript{3}-polluted and non-O\textsubscript{3}-polluted months (Fig. S3), suggesting that O\textsubscript{3} formation was sensitive to VOCs, and thus the reductions of the emissions of VOCs will be beneficial for O\textsubscript{3} alleviation.

3.2.2 Contribution of VOCs to OFP and SOAFP

As discussed in Sect. 3.2.1, O\textsubscript{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-
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/NOx was generally below 3 during the sampling period, indicating high NOx 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; Ackagi 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$_3$
compliance days and 16% on O₃ pollution days) compared with the non-O₃-polluted months (8% and 13%, respectively). During the O₃-polluted months, the contributions of industrial emissions (22%) and fuel evaporation (18%) on O₃ pollution days were much higher than those on O₃ compliance days (18% and 13%, respectively). Figure 9 presents the relative contributions of individual VOC sources from PMF to OFP. On the basis of O₃ formation impact, diesel and gasoline vehicle exhaust were major contributors. During the O₃-polluted months, vehicle emissions and fuel evaporation showed higher OFP values on O₃ pollution days (93.9 and 35.5 µg m⁻³) compared with those on O₃ compliance days (88.0 and 25.8 µg m⁻³, respectively). Although industrial emissions act as an important source for VOC concentrations on O₃ pollution days (shown in Fig. 8), the potential to form O₃ 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 O₃ formation potentials. Such results suggested that the fuel use and diesel vehicle exhaust should be preferentially controlled for O₃ mitigation.

The PM₂.₅-polluted months showed higher proportions of industrial (29% on both PM₂.₅ compliance and PM₂.₅ pollution days) as well as coal and biomass combustion emissions (16% on PM₂.₅ compliance days and 18% on PM₂.₅ pollution days) compared with the non-PM₂.₅-polluted months (17% and 10%, respectively). The PM₂.₅ pollution days were dominated by industrial emission (29%), diesel vehicle exhaust (24%), and combustion sources (18%). During the PM₂.₅-polluted months, the contribution of diesel vehicle exhaust on PM₂.₅ pollution days (24%) was higher than that on PM₂.₅ compliance days (16%). On the basis of PM₂.₅ formation impact, diesel vehicle exhaust and combustion were two major contributors on PM₂.₅ pollution days (shown in Fig. 9), and these two sources showed obvious higher SOAFP on PM₂.₅ pollution days (0.30 and 0.32 µg m⁻³, respectively) compared with those on PM₂.₅ compliance days.

Figure 6. Ratios of i- to n-pentane and toluene to benzene at different PM₂.₅ and O₃ levels.

![Figure 6](https://example.com/figure6.png)

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

![Figure 7](https://example.com/figure7.png)
Figure 8. Contributions of each source to VOCs on (a) O₃ compliance days during the O₃-polluted months, (b) O₃ pollution days during the O₃-polluted months, and during (c) the non-O₃-polluted months. Contributions of each source to VOCs on (d) PM₂.₅ compliance days during the PM₂.₅-polluted months, (e) PM₂.₅ pollution days during the PM₂.₅-polluted months, and (f) during the non-PM₂.₅-polluted months.

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

of the PM₂.₅-polluted months (0.15 and 0.14 µg m⁻³, respectively). Although industrial emissions act as an important source for VOC concentrations on PM₂.₅-pollution days, the potential to form PM₂.₅ 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 PM₂.₅ pollution.

Based on the mass concentrations of individual species in each source, the following were the dominant species contributing to photochemical O₃ 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 PM₂.₅ 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 O₃ and SOA formation across different seasons. It should be pointed out that the sampling campaign for VOC measurements 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 O₃ and PM₂.₅ occurred, respectively. The variations, sources, and secondary transformation potentials of VOCs, particularly for O₃ and PM₂.₅ 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 O₃ levels during the O₃-polluted months were higher than during the non-O₃-polluted months, and a similar pattern was found for PM₂.₅. The molar ratio of VOCs to NOₓ indicated that O₃ formation was limited by VOCs during both the O₃-polluted non-O₃-polluted months, and thus reducing VOC emissions is essential for allevia-
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).

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