Measurement report: Ambient volatile organic compounds (VOCs) pollution at urban Beijing: characteristics, sources, and implications for pollution control

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Abstract

The increasing ozone (O_3) pollution and high fraction of secondary organic aerosols (SOA) in fine particle mass 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 of 2018 to 17 January of 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 VOCs 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 TVOCs 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 VOCs sources during both the O_3-polluted and $PM_{2.5}$-polluted months. On the base 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 for alleviating O_3 pollution. Instead, VOCs from diesel exhaust and coal/biomass combustion were found to be the dominant contributors for 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 government to formulate effective VOCs control measures for air pollution in Beijing.

Key words: VOCs, OFP, SOAFP, Source appointment

1. Introduction

The 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 Ecolgy (MEE) network has witnessed an upward trend for O_3 across the country over the period 2013-2019 (Fu et al., 2019; Li et al., 2017; Li et al., 2020; Shen et al., 2019; Fan et al., 2020). Besides, haze pollution occurred in urban sites in recent years were commonly characterized by enhanced formation of secondary organic aerosols (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; Li et al., 2017b; Sun et al., 2020; 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, the O_3 formation was generally VOCs-limited, and it is suggested that VOCs emission control is necessary for effective alleviation of photochemical smog (Liu et al., 2020a,b; Shao et al., 2009; Wang et al., 2020; Xing et al., 2011). Besides, the VOCs compounds including aromatics and biogenic species have significant impact on SOA formation which play an important role in haze formation (Huang et al., 2014; Tong et al., 2021). VOCs 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 VOCs sources in urban Shanghai and urban Guangzhou, while the primary sources of VOCs in Wuhan, Zhengzhou and Beijing cities are combustion and vehicle exhaust (Han et al., 2020; Shen et al., 2020; Liu et al., 2020a; Li et al., 2019a). Apart from the diversity of emission sources, different VOCs species exhibited different propensities to form O_3 and SOA. Observation-based studies commonly applied 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 and 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 of concentrations, sources as well as the influence of photochemical reactions of VOCs on annual scale was still limited. Besides, most of the available reports on VOCs 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 OVOC also participate actively in chemical reactions related to secondary formation (Li et al., 2019a; Zhao et al., 2020; Yang et al., 2018; Sinha and Sinha., 2019). Therefore, the long-term and comprehensive monitoring of VOCs are 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 (Wang et al., 2014a; Wang et al, 2017; Li et al., 2019d; 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 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 (**错误!超链接引用无效。**, making Beijing the top city in China in terms of number of motor vehicles. The existing field measurements in Beijing were mostly conducted before 2016, and the observation in most recent years is quite limited (Li et al., 2015; Li et al., 2019c; Liu et al., 2020a; 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, respectively. 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 on 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 policymakers to alleviate ozone and haze pollution in Beijing.

2. Methodology

2.1 Field measurement

The sampling site is at the roof of a three-floor building on the campus of Tsinghua University (40.00°N, 116.33°E), northwest of Beijing urban area (Fig. S1). The altitude of the sampling site is 57 m. This sampling site is surrounded by school and there are no large emission sources nearby, therefore it can represent the urban air quality in Beijing. Details of the site description is found in 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. The samples were pre-processed 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). Pressure gage was used to test if the canister has air leakage exist before sampling every time, and blanks were prepared using cleaned canisters to fill with high purity nitrogen. The cryotraps of precooling system was baked before analyses each day and between every samples. 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 VOCs measurement are 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 °C for 3 minutes initially, then raised to 90 °C at 8°C per minute, and later raised to 220 °C at 6°C per minute, holding for 9 minutes. In this work, 95 target VOCs, including 25 alkanes, 8 alkenes, 16 aromatics, 34 halocarbons and 12 OVOC were quantified. It should be noted that VOCs compounds (C2-C3) with 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 US EPA TO-15 standard was used to construct the calibration curves for the target VOCs. Quality assurance and quality control, including method detection limit (MDL) of each compound, laboratory and field blanks, retention time, accuracy and duplicate measurements of samples were performed according to USEPA Compendium Method TO-15 (USEPA 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 were 0.5%-6.0%. Previous field measurements have reported that the precision of 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 the the Pulsed Fluorescence SO_2 Analyzer (Thermo Fisher Scientific USA, 43I), Chemiluminescence NO–NO_2-NO_X Analyzer (Thermo Fisher Scientific USA, 17I) and ultra-violet (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) (Wang et al., 2014a). 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/forestcasts/datasets/browse-reanalysis -datasets).

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 VOCs species and sources in secondary formation, which were estimated using Eqs. (1) and (2).

$$OFP = \sum\nolimits_{\mathrm{i}}^{n} MIR_i \times \ [VOC(ppb)]_i \tag{1}$$

$$SOAFP = \sum\nolimits_{i}^{n} Y_i \times [VOC(ppb)]_i \tag{2}$$

where *n* represents the number of VOCs, [VOC]*i* represents the *i*th VOC species concentration, MIR*i* is the maximum incremental reactivity for the *i*th VOC species, and *Yi* is the SOA yield of VOC_i (McDonald et al., 2018). The MIR for each VOC species were 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 modelling relates the hourly variability of O_3 and $PM_{2.5}$ to that of meteorological variables. The model performance was evaluated through 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 ten 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, RMSE, and 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 VOCs source apportionment (Abeleira et al., 2017; Li et al., 2019a; Xue et al., 2017). The detailed description of the PMF model is found elsewhere (Ling et al., 2011; Yuan et al., 2009). 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 of below 2 were excluded. Based on this, 53 VOC species including source tracers (e.g., chloromethane, trichloroethylene, tetrachloroethylene and MTBE) 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 of $\text{Unc} = 5/6 \times \text{MDL}$; if the concentration is greater than the MDL provided, the uncertainty is calculated as $\text{Unc} = [(\text{error faction} \times \text{mixing ratio})^2 + (\text{MDL})^2]1/2$.

During the PMF analysis, the bootstraps (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 gained 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°C 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 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 TVOCs 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 TVOCs 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., 2020a; Li et al., 2015b), indicating the effectiveness of control measures in most recent years on lowering VOCs emission. Besides, the composition of major chemical groups also showed remarkable changes, with decreased proportions of alkanes while increased fractions of halocarbons, aromatics and OVOCs, reflecting the changes in emission sources types in most recent years.

During the measurement period, 14 O_3 pollution episodes (days with maximum 8-h average O_3 exceeding 160 μg m^{-3}) were observed on 17 April, 3-4 May, 16 May, 19-20 June, 24-25 June, 2July, 5 July, 13 July, 25-26 September and and 28 September of 2019, respectively. The comparison of meteorological parameters and air pollutants on O_3 pollution and compliance days (days with maximum 8-h average O_3 below 160 μg m^{-3}) duringf the five 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 O_3 pollution days (1.31 ± 0.90 m s^{-1}) was slightly lower than that on O_3 compliance days (1.47 ± 1.10 m s^{-1}), indicating that precursors were more conductive to be diluted on O_3 compliance days. The variation trend of O_3 and temperature displayed the negative correlation, and the linear correlations between O_3 and temperature on O_3 pollution days ($R^2 = 0.63$) was stronger than that on O_3 compliance days ($R^2 = 0.35$). The mean TVOC concentration on O_3 pollution days (32.3 ppbv) was higher than that on O_3 compliance days (29.6 ppbv), which was mainly attributed to higher concentrations of MTBE, acrolein, trans-2-butene r 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/gas evaporation (Li et al., 2019a). Such result suggested enhanced contribution of traffic emissions on O_3 pollution days. Besides, the concentration of isoprene, which is primarily produced by vegetation through photosynthesis, increased significantly on O_3 pollution days probably due to the stronger plant emission at elevated temperature (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; Wang et al., 2013a). The mean X/E value on O_3 compliance days (1.41) was higher than that on O_3 pollution days (1.17), indicating enhanced secondary transformation of VOCs on O_3 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 of 2019, 1-2 December and 5 December of 2018, respectively. During the six $PM_{2.5}$-polluted months (i.e., December of 2018, January, April, May, October and November of 2019), the WS on $PM_{2.5}$ pollution days (1.05 ± 1.06 m s^{-1}) was lower than that on $PM_{2.5}$ compliance days (1.43 ± 1.06 m s^{-1}), indicating the weaker ability of winds for the dilution and diffusion of precursor 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 on 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, of which concentrations 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 section 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 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 μg m^{-3}) was significantly higher than that on O_3 compliance days (35.3 μg m^{-3}). After removing the meteorological contribution, the residual emission-driven O_3 level on O_3 pollution (45.3 μg m^{-3}) and compliance days (44.9 μg m^{-3}) of the O_3-polluted months was almost identical and were significantly higher than that during the non-O_3-polluted months (23.8 μg 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 μg m^{-3}) > $PM_{2.5}$ compliance days of the $PM_{2.5}$-polluted months (44 μg m^{-3}) > non-$PM_{2.5}$-polluted months (29 μg m^{-3}). These results suggested 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 the O_3 formation is VOC limited or NO_X limited (Li et al., 2019a). Generally, VOC-sensitive regime occurs when VOCs/NO_X ratios are below 10 while 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 the 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 3.1, O_3 formation was generally VOCs-sensitive during the measurement period. Quantifying the contribution of speciated VOCs species to O_3 is helpful for developing effective VOCs control measures and alleviating O_3 pollution. The averaged 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 were 224.9, 201.4, and 187.5 μg m^{-3}, respectively (Fig. 5). According to our observations, the higher OFP on O_3 pollution days than that 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 that in 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%), respectively.

As shown in Fig. S3, the ratio of VOCs/NOx 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 SOAFP 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 six $PM_{2.5}$-polluted months, the higher SOAFP on $PM_{2.5}$ pollution days than that 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 on $PM_{2.5}$ 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%), respectively.

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 the photochemical processing and the emission inputs, and ratios of VOCs species having similar atmospheric lifetimes can reflect the source features (Li et al., 2019a; Raysoni et al., 2017 Song et al., 2021). The ratio of *i*-pentane to *n*-pentane are widely used to examine the impact of vehicle emissions, fuel evaporation and combustion emissions, within the i/n-pentane ratios of ranging between 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; Wang et al., 2013b; 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 the 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 between 1.7-2.1, suggesting the significant impact of fuel evaporation.

The toluene/ benzene (T/ B) ratio, 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; Wang et al., 2013c; Yao et al., 2013; Zhang et al., 2013; Yao et al., 2015a; 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; Wang et al.,2014b; 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 is presented in Fig. 7 and Fig. 8, respectively. Six emission sources were identified: coal/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 VOCs 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, and 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 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 base 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 μg m^{-3}) compared with those on O_3 compliance days (88.0 and 25.8 μg m^{-3}, respectively). Although industrial emissions act as an important source for VOCs 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 while 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 controlled preferentially for O_3 mitigation.

The $PM_{2.5}$-polluted months showed higher proportions of industrial (29% on both $PM_{2.5}$ compliance and $PM_{2.5}$ pollution days) and coal/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 source (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 base 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 μg m^{-3}, respectively) compared with those on $PM_{2.5}$ compliance days 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 VOCs 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 controlled preferentially for alleviating $PM_{2.5}$ pollution.

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

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 VOCs measurement was not conducted continuously during December 2018 and November 2019. For instance, the air samples were not collected in August and February-March of 2019, during which the 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 remained, the results obtained in this study provide useful information for VOCs emission control strategy and assist overcoming air pollution issue in Beijing.

4. Conclusions

In this work, the field sampling campaign of VOCs was conducted at urban Beijing from December 2018 to November 2019. The VOCs concentrations ranged from 5.5 to 118.7 ppbv with mean value of 34.9 ppbv. Alkanes, OVOCs and halocarbons were the dominant chemical groups, accounting for 75-81% of the TVOCs across the sampling months. By excluding the meteorological impact, the emission-driven O_3 level during the O_3-polluted months were higher than that during the non-O_3-polluted months, and 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 VOCs emission is essential for alleviation of O_3 pollution. The contributions of coal/biomass combustion, solvent use, industrial sources, oil/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 VOCs 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 for alleviating 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

The meteorological data are available at http: //data.cma.cn/ (China Meteorological Administration). The website can be browsed in English http://data.cma.cn/en. The concentrations of air pollutants including $PM_{2.5}$, O_3 and NO_X are available at https://air.cnemc.cn:18007/ (Ministry of Ecology and Environment the People's Republic of China). The website can be browsed in English http://english.mee.gov.cn/. The daily mixing ratio of individual VOCs species is given in Table S1 in the Supplement.

Author Contributions

DW designed the study and performed the VOCs measurement. QX and RH assists 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 authors declare that they have no conflict of interest.

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Figure captions

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).

Figure 3. The averaged levels of temperature (T), wind speed (WS), and O_3 and NO_X concentrations on (a) O_3 compliance during the O_3-polluted months, (b) O_3 pollution days during the O_3-polluted months, and (c) differences in VOCs 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 during the $PM_{2.5}$-polluted months, (e) $PM_{2.5}$ pollution days during the $PM_{2.5}$-polluted months, and (f) differences in VOCs 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.

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

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

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

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.

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, and SOAFP values for the $PM_{2.5}$ pollution (c) and compliance (d) days of the $PM_{2.5}$-polluted months.

Figure. 1.

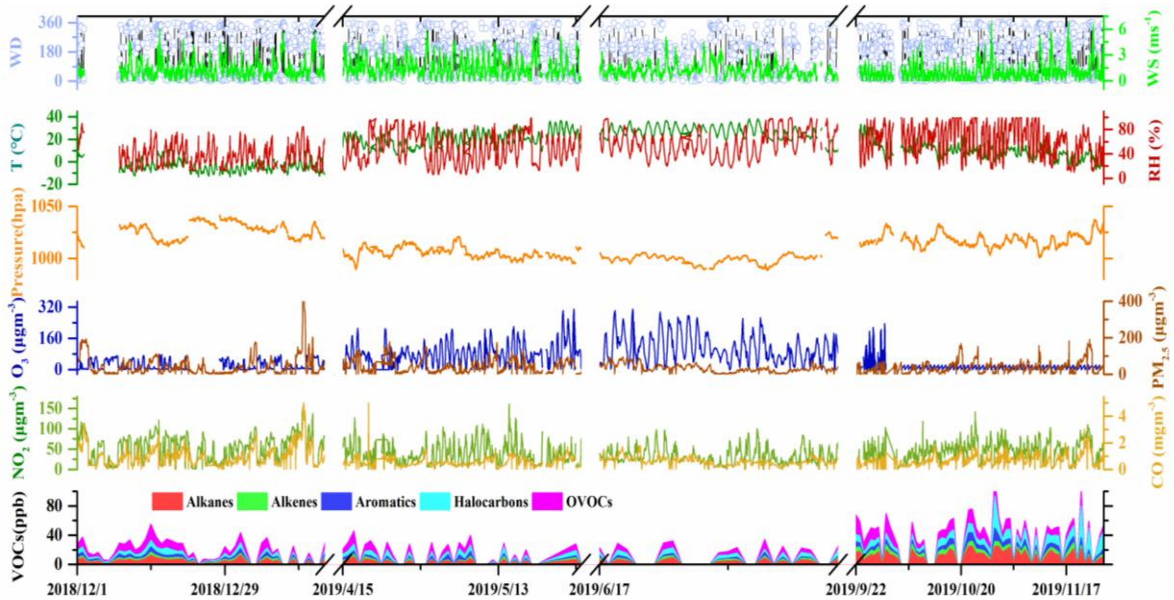

WD
360
180
0
WS (ms-1)
6
3
0
T (°C)
40
20
0
-20
RH (%)
80
40
0
Pressure(hpa)
1050
1000
O3 (μgm-3)
320
160
0
PM2.5 (μgm-3)
400
200
0
NO2 (μgm-3)
150
100
50
0
CO (mgm-3)
4
2
0
VOCs(ppb)
80
40
0
Alkanes
Alkenes
Aromatics
Halocarbons
OVOCs
2018/12/1
2018/12/29
2019/4/15
2019/5/13
2019/6/17
2019/9/22
2019/10/20
2019/11/17

Figure 2.

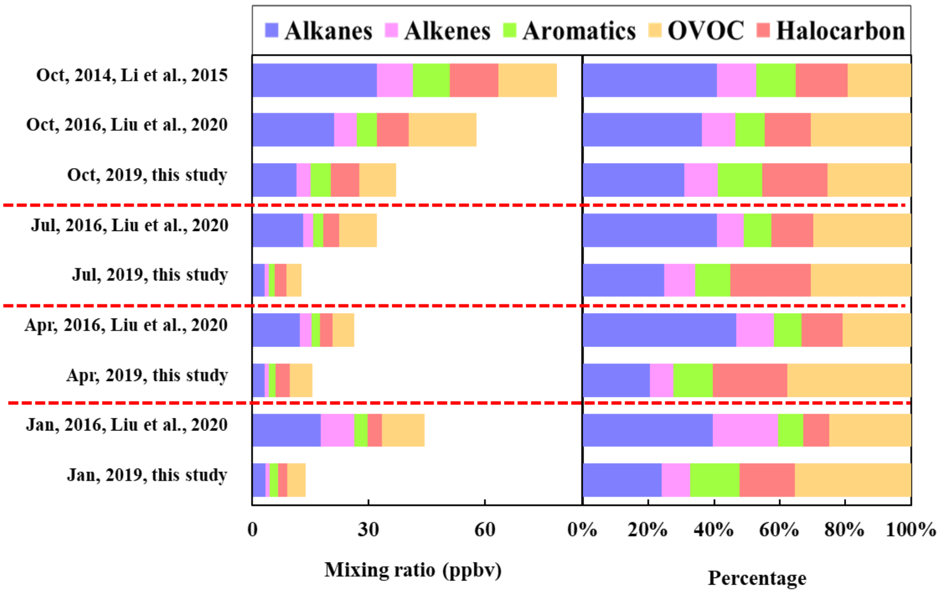

Alkanes
Alkenes
Aromatics
OVOC
Halocarbon
Oct, 2014, Li et al., 2015
Oct, 2016, Liu et al., 2020
Oct, 2019, this study
Jul, 2016, Liu et al., 2020
Jul, 2019, this study
Apr, 2016, Liu et al., 2020
Apr, 2019, this study
Jan, 2016, Liu et al., 2020
Jan, 2019, this study
0
30
60
Mixing ratio (ppbv)
0%
20%
40%
60%
80%
100%
Percentage

Figure. 3.

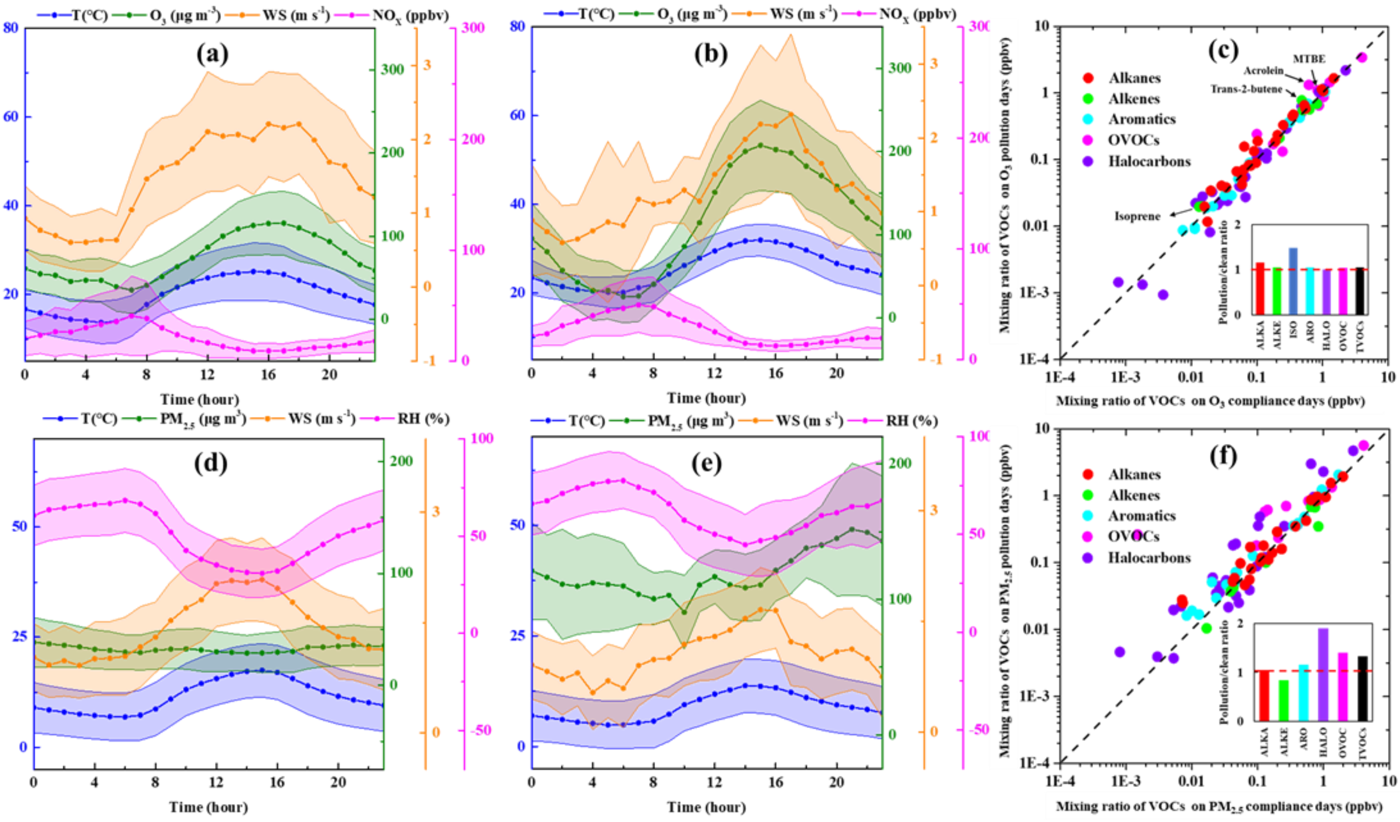
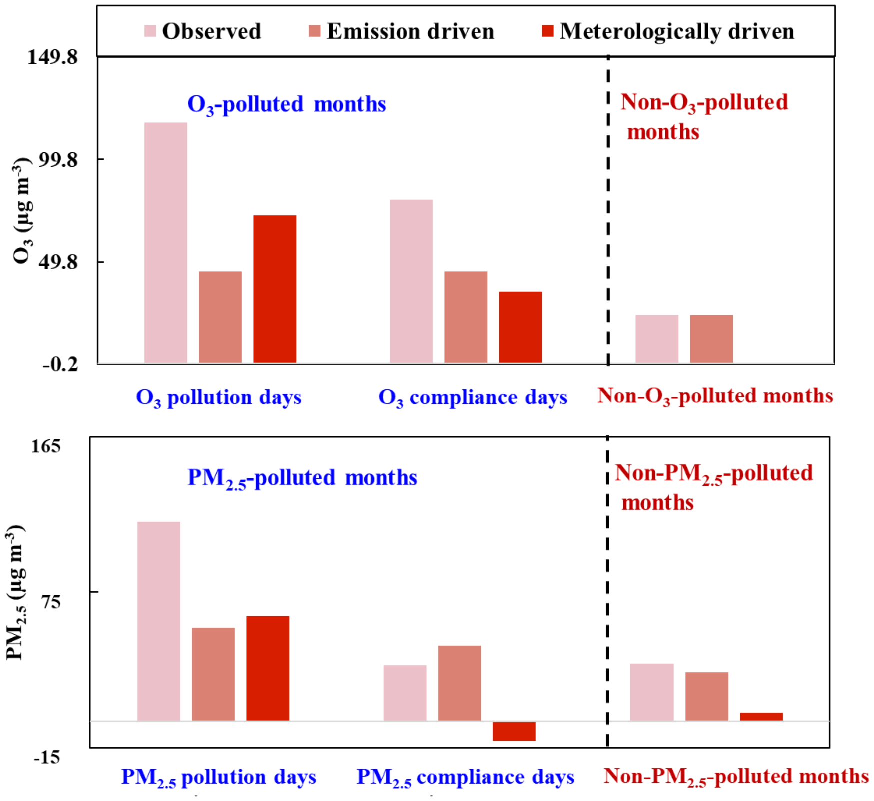

(a)
(b)
(c)
(d)
(e)
(f)
T(°C)
O3 (μg m-3)
WS (m s-1)
NOx (ppbv)
PM2.5 (μg m3)
RH (%)
Time (hour)
Alkanes
Alkenes
Aromatics
OVOCs
Halocarbons
MTBE
Acrolein
Trans-2-butene
Isoprene
Mixing ratio of VOCs on O3 pollution days (ppbv)
Mixing ratio of VOCs on O3 compliance days (ppbv)
Mixing ratio of VOCs on PM2.5 pollution days (ppbv)
Mixing ratio of VOCs on PM2.5 compliance days (ppbv)
Pollution/clean ratio
ALKA
ALKE
ISO
ARO
HALO
OVOC
TVOCs

Figure. 4



Observed
Emission driven
Meterologically driven
149.8
99.8
49.8
-0.2
O₃ (μg m⁻³)
O₃-polluted months
Non-O₃-polluted months
O₃ pollution days
O₃ compliance days
Non-O₃-polluted months
165
75
-15
PM₂.₅ (μg m⁻³)
PM₂.₅-polluted months
Non-PM₂.₅-polluted months
PM₂.₅ pollution days
PM₂.₅ compliance days
Non-PM₂.₅-polluted months

Figure. 5

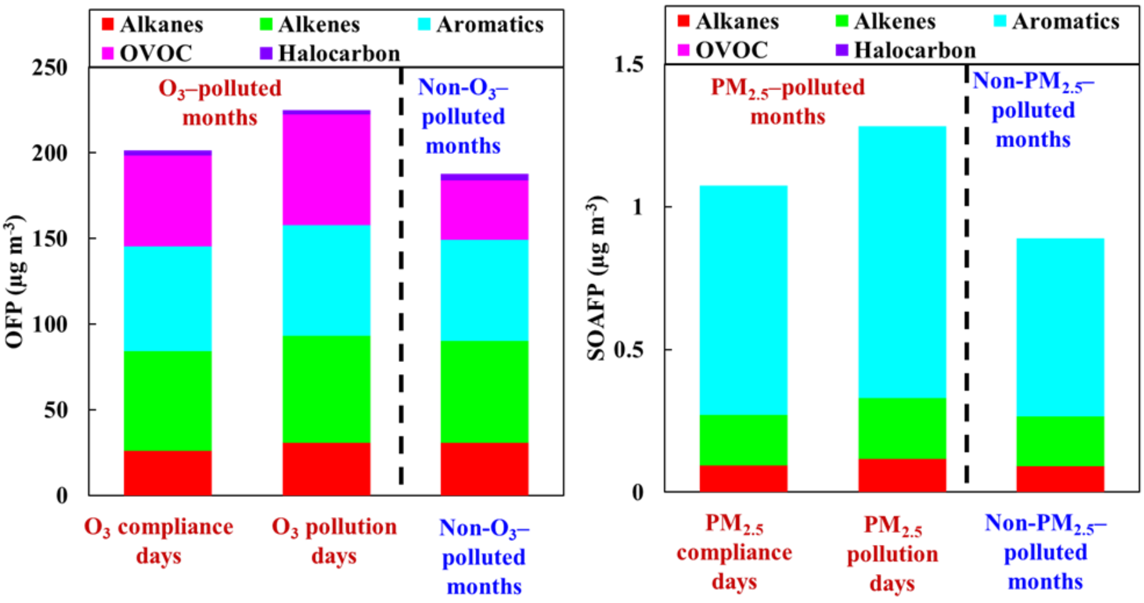
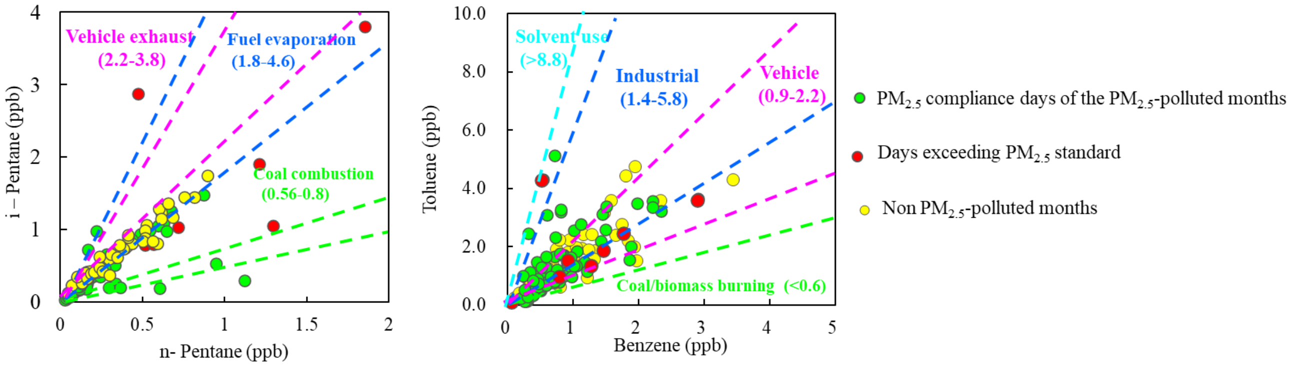

Alkanes
Alkenes
Aromatics
OVOC
Halocarbon
OFP (μg m^{-3})
250
200
150
100
50
0
O$_3$–polluted months
Non-O$_3$–polluted months
O$_3$ compliance days
O$_3$ pollution days
Non-O$_3$–polluted months
Alkanes
Alkenes
Aromatics
OVOC
Halocarbon
SOAFP (μg m^{-3})
1.5
1
0.5
0
PM$_{2.5}$–polluted months
Non-PM$_{2.5}$–polluted months
PM$_{2.5}$ compliance days
PM$_{2.5}$ pollution days
Non-PM$_{2.5}$–polluted months

Figure. 6

Ratios of i/*n*-pentane and toluene/benzene at different $PM_{2.5}$ levels



Ratios of i/*n*-pentane and toluene/benzene at different O_3 levels

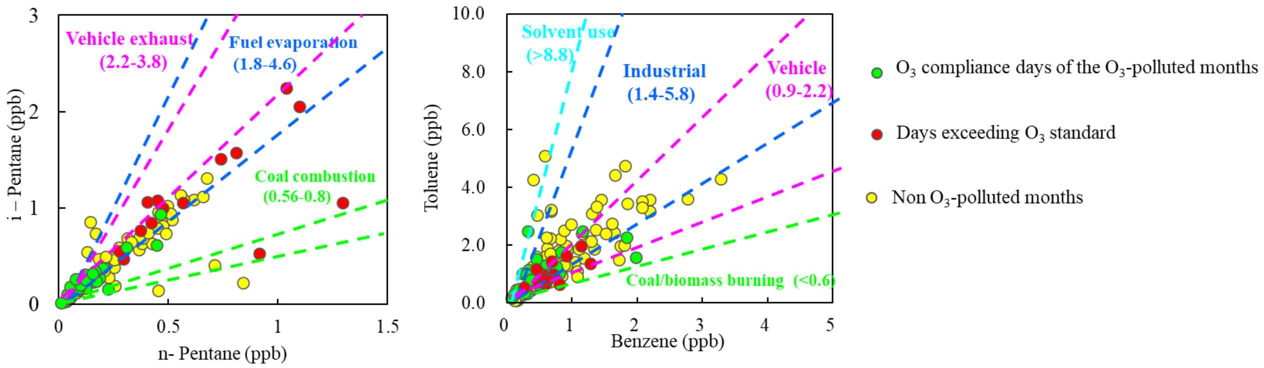


Figure. 7.

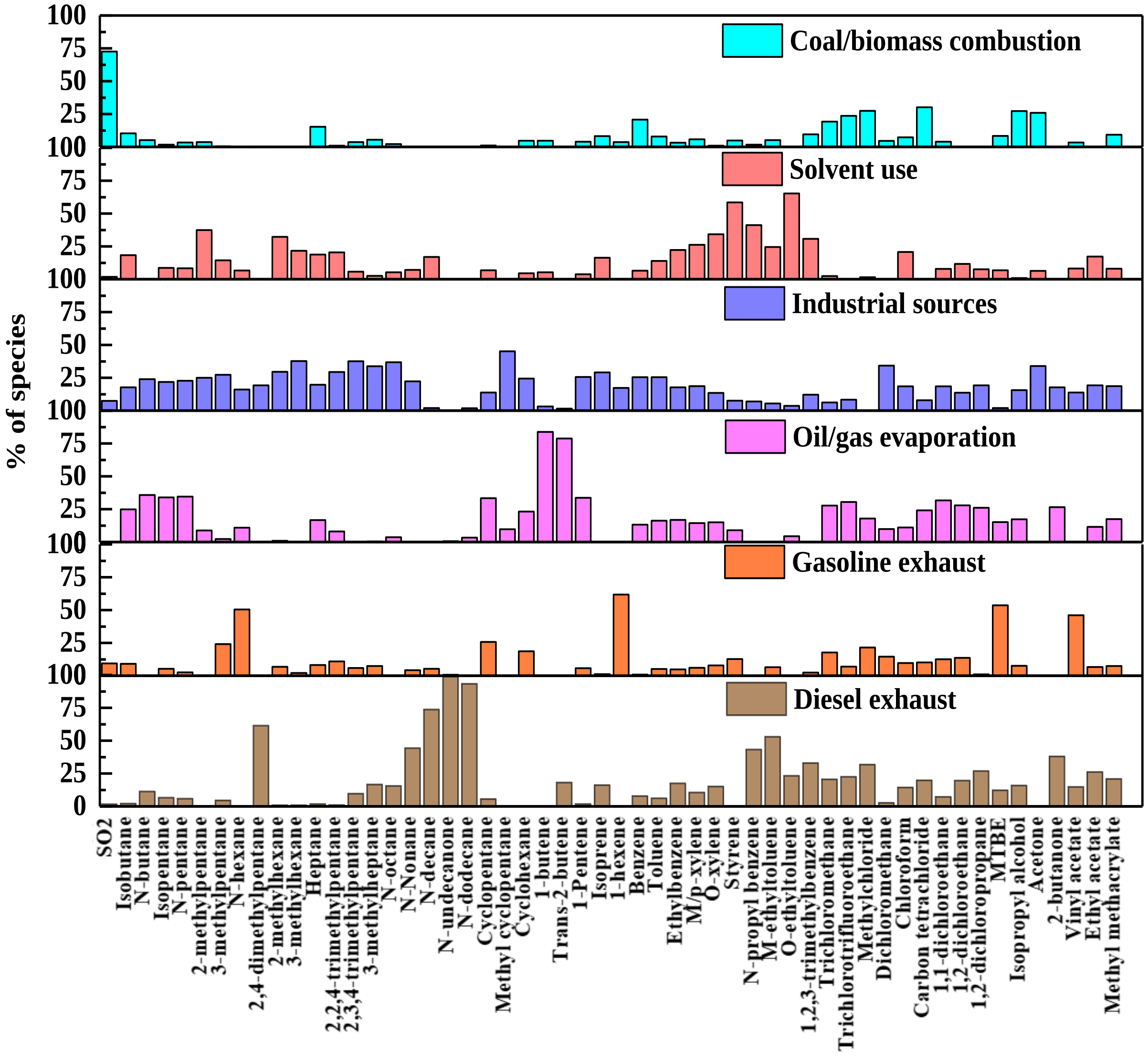

Coal/biomass combustion
Solvent use
Industrial sources
Oil/gas evaporation
Gasoline exhaust
Diesel exhaust
% of species
100
75
50
25
0
SO2
Isobutane
N-butane
Isopentane
N-pentane
2-methylpentane
3-methylpentane
N-hexane
2,4-dimethylpentane
2-methylhexane
3-methylhexane
Heptane
2,2,4-trimethylpentane
2,3,4-trimethylpentane
3-methylheptane
N-octane
N-Nonane
N-decane
N-undecanone
N-dodecane
Cyclopentane
Methyl cyclopentane
Cyclohexane
1-butene
Trans-2-butene
1-Pentene
Isoprene
1-hexene
Benzene
Toluene
Ethylbenzene
M/p-xylene
O-xylene
Styrene
N-propyl benzene
M-ethyltoluene
O-ethyltoluene
1,2,3-trimethylbenzene
Trichloromethane
Trichlorotrifluoroethane
Methylchloride
Dichloromethane
Chloroform
Carbon tetrachloride
1,1-dichloroethane
1,2-dichloroethane
1,2-dichloropropane
MTBE
Isopropyl alcohol
Acetone
2-butanone
Vinyl acetate
Ethyl acetate
Methyl methacrylate

Figure. 8

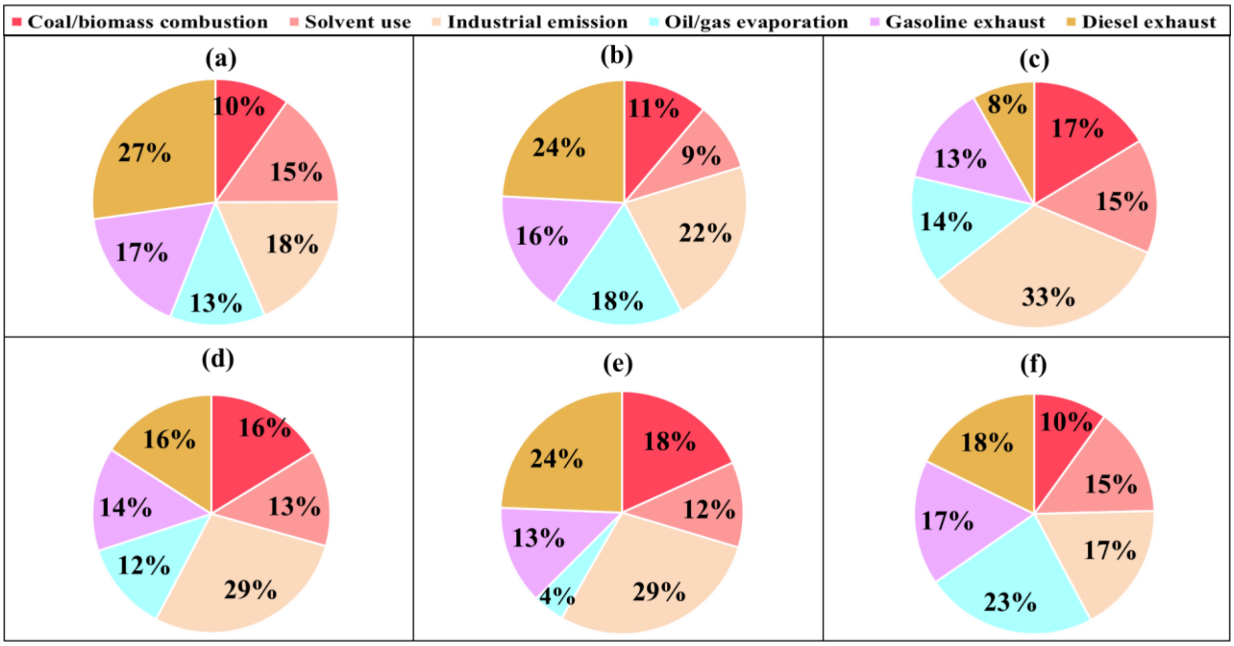
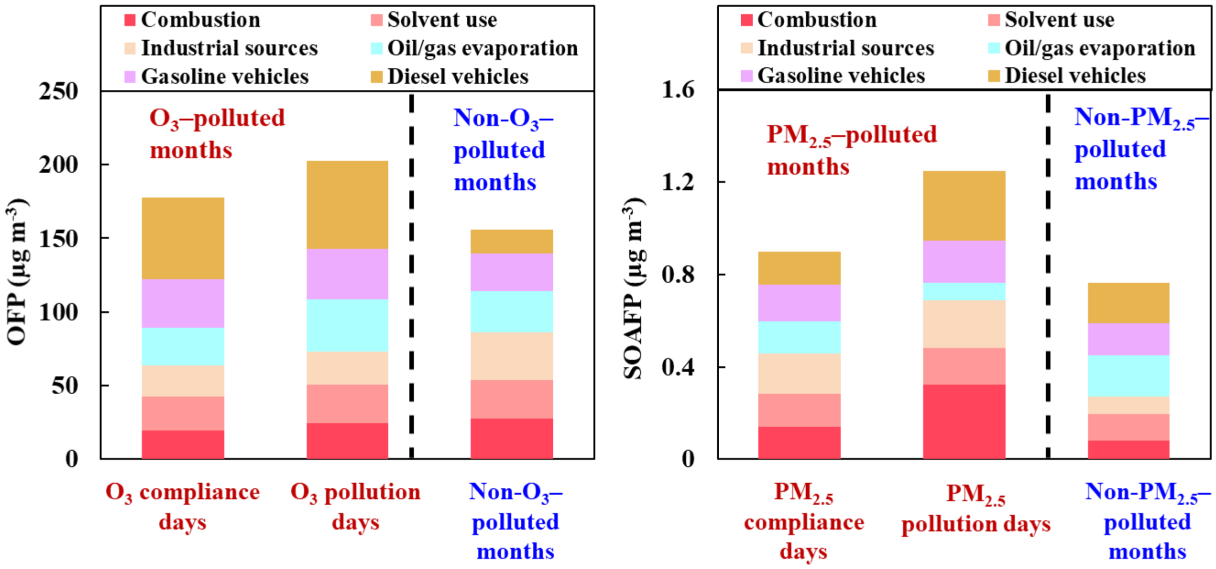
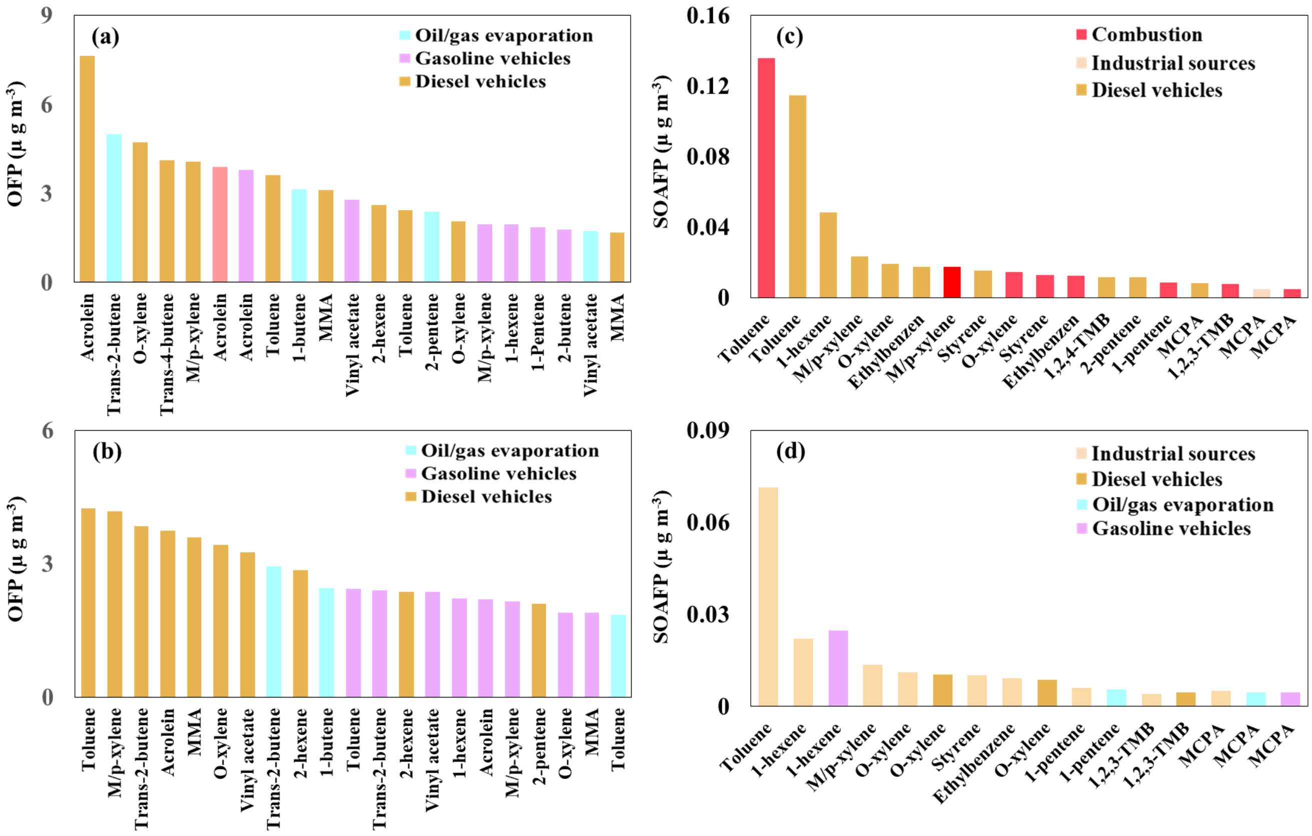

Coal/biomass combustion
Solvent use
Industrial emission
Oil/gas evaporation
Gasoline exhaust
Diesel exhaust
(a)
10%
15%
18%
13%
17%
27%
(b)
11%
9%
22%
18%
16%
24%
(c)
17%
15%
33%
14%
13%
8%
(d)
16%
13%
29%
12%
14%
16%
(e)
18%
12%
29%
4%
13%
24%
(f)
10%
15%
17%
23%
17%
18%

Figure. 9



Combustion
Solvent use
Industrial sources
Oil/gas evaporation
Gasoline vehicles
Diesel vehicles
OFP (μg m^{-3})
0
50
100
150
200
250
O_3–polluted months
Non-O_3–polluted months
O_3 compliance days
O_3 pollution days
Non-O_3–polluted months
SOAFP (μg m^{-3})
0
0.4
0.8
1.2
1.6
$PM_{2.5}$–polluted months
Non-$PM_{2.5}$–polluted months
$PM_{2.5}$ compliance days
$PM_{2.5}$ pollution days
Non-$PM_{2.5}$–polluted months

Figure. 10


(a)
OFP (μ g m^{-3})
9
6
3
0
Oil/gas evaporation
Gasoline vehicles
Diesel vehicles
Acrolein
Trans-2-butene
O-xylene
Trans-4-butene
M/p-xylene
Acrolein
Acrolein
Toluene
1-butene
MMA
Vinyl acetate
2-hexene
Toluene
2-pentene
O-xylene
M/p-xylene
1-hexene
1-Pentene
2-butene
Vinyl acetate
MMA
(c)
SOAFP (μ g m^{-3})
0.16
0.12
0.08
0.04
0
Combustion
Industrial sources
Diesel vehicles
Toluene
Toluene
1-hexene
M/p-xylene
O-xylene
Ethylbenzen
M/p-xylene
Styrene
O-xylene
Styrene
Ethylbenzen
1,2,4-TMB
2-pentene
1-pentene
MCPA
1,2,3-TMB
MCPA
MCPA
(b)
OFP (μ g m^{-3})
6
3
0
Oil/gas evaporation
Gasoline vehicles
Diesel vehicles
Toluene
M/p-xylene
Trans-2-butene
Acrolein
MMA
O-xylene
Vinyl acetate
Trans-2-butene
2-hexene
1-butene
Toluene
Trans-2-butene
2-hexene
Vinyl acetate
1-hexene
Acrolein
M/p-xylene
2-pentene
O-xylene
MMA
Toluene
(d)
SOAFP (μ g m^{-3})
0.09
0.06
0.03
0
Industrial sources
Diesel vehicles
Oil/gas evaporation
Gasoline vehicles
Toluene
1-hexene
1-hexene
M/p-xylene
O-xylene
O-xylene
Styrene
Ethylbenzene
O-xylene
1-pentene
1-pentene
1,2,3-TMB
1,2,3-TMB
MCPA
MCPA
MCPA