



Variability and Sources of Ambient Volatile Organic Compounds Based on Online Measurements in a Suburban Region of Nanjing, Eastern China

Rongrong Wu¹, Yu Zhao^{1,2*}, Jie Zhang^{2,3}, Lei Zhang¹

¹ State Key Laboratory of Pollution Control & Resource Reuse and School of the Environment, Nanjing University, Nanjing, Jiangsu 210023, China

² Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, CICAET, Nanjing, Jiangsu 210044, China

³ Jiangsu Provincial Academy of Environmental Science, Nanjing, Jiangsu 210036, China

ABSTRACT

Volatile organic compounds (VOCs) are the key precursors of ozone (O₃) and secondary organic aerosol (SOA) formation. To identify the variation in VOCs emission sources, simultaneous VOCs measurements were conducted for one year at a suburban site (Xianlin Campus of Nanjing University (NJU)) in Nanjing, a highly polluted city of the Yangtze River Delta (YRD) region in China. The annual average concentration of VOCs at NJU was observed to be 18.95 ± 14.95 ppbv, with alkanes, alkenes and aromatics contributing 67.5%, 13.6% and 18.9%, respectively, of the total mass concentration. The ratios for *i*-pentane/*n*-pentane and *m,p*-xylene/ethylbenzene showed that the ambient VOCs at NJU were affected by fuel evaporation and long-distance transport. A positive matrix factorization (PMF) model was applied for source apportionment of the VOCs, and seven factors were identified. Vehicle exhaust, evaporation, natural gas (NG) and aged air masses, combustion and synthetic industries, solvents and painting, petrochemical plants and mixed industrial sources were estimated to contribute 23.5%, 16.3%, 15.9%, 14.6%, 13.2%, 10.8% and 5.6%, respectively. The contribution from traffic emissions (i.e., vehicle exhaust) exceeded that suggested by a local emission inventory (9.7%). The concentration-weighted trajectory (CWT) model revealed that the highly polluted air masses arriving at NJU originated in the industrial areas of northeastern Nanjing and the YRD. The contributions from petrochemical plants, solvents and painting, and aged air masses were found to be increased during O₃ and PM_{2.5} pollution days in suburban areas, indicating the importance of reducing industrial emissions and jointly controlling VOCs on a regional scale.

Keywords: VOCs; Source apportionment; Positive matrix factorization; Pollution episodes.

INTRODUCTION

As the key precursors of ozone (O₃) and secondary organic aerosol (SOA) formation, volatile organic compounds (VOCs) lead to severe air pollution (Huang *et al.*, 2014; Lyu *et al.*, 2016; Wu and Xie, 2017) and, thereby, cause damage to human health (WHO, 2003). Although biogenic emissions dominate at the global scale (Guenther *et al.*, 2006), anthropogenic sources are more influential at the regional and urban scales (Zhao *et al.*, 2017). Due to the uneven distribution of human activities and the associated emission sources, there is significant variability in the spatial and temporal distribution of individual VOCs, influencing the secondary pollutant formation and causing difficulties in

creating strategies for the control of precursors (Latif *et al.*, 2012; Jiang *et al.*, 2018). Therefore, a better understanding of VOCs sources is important for regional and urban air quality improvement.

With rapid economic development in China, air pollution with high levels of ozone (O₃) and fine particulates (PM_{2.5}) has been widely reported in many regions (He *et al.*, 2017). The emissions of anthropogenic VOCs, the key precursors of ambient O₃ and PM_{2.5}, have doubled during the past two decades (Zhao *et al.*, 2017). Previous studies have been conducted to analyze the characteristics and identify the sources of ambient VOCs using receptor models on megalopolis clusters such as the Beijing-Tianjin-Hebei (BTH) region (Li *et al.*, 2015; Wang *et al.*, 2015), the Yangtze River Delta (YRD) region (Mo *et al.*, 2017; Zhu *et al.*, 2018) and the Pearl River Delta (PRD) region (Zhang *et al.*, 2015; Mo *et al.*, 2018; Ou *et al.*, 2018) in China. For example, An *et al.* (2014) used principal component analysis/absolute principal component scores (PCA/APCS) to investigate VOCs sources at an industrial site in Nanjing. However, the variation in the

* Corresponding author.

Tel.: 86-25-89680650

E-mail address: yuzhao@nju.edu.cn

VOCs sources might be different for suburban areas. In the PRD region, for example, gridded measurements of VOCs were conducted, and spatial discrepancies in VOCs sources were observed (Mo *et al.*, 2018; Ou *et al.*, 2018). A larger contribution of industrial processes was found in the industrial area, while a larger contribution of gasoline-related sources was found in suburban zones. To comprehensively evaluate the influence of atmospheric VOCs on air quality and to further identify the sources, further measurements of ambient VOCs at other functional areas are still needed.

A few studies have shown various sources of VOCs during pollution days. Sun *et al.* (2016) calculated the SOA formation potentials of VOCs during the winter haze period in Beijing and found that emissions from vehicles, chemical industries and solvents were the main causes of elevated VOCs. Wu *et al.* (2016) suggested that extremely high levels of VOCs during the haze event could be primarily attributed to vehicular emissions, biomass burning and regional transport and were aggravated by unfavorable meteorological conditions. However, most studies of pollution events have focused on particulate matter (PM) and those focusing on O₃ are still limited. In most developed regions of China, air pollution with high levels of O₃ and PM has become one of the most severe environmental pollution issues (Huang *et al.*, 2014; Xu *et al.*, 2018), and O₃ has gradually replaced PM to be the major pollutant in summer (MEP, 2018). Therefore, studies on the characteristics and source variations of VOCs on O₃ and PM pollution days are urgently needed to help provide scientific support, enabling the government to formulate effective air pollution control measures.

Nanjing is a typical developed city in the YRD region of eastern China with intensive chemical industries. The annual emissions of anthropogenic VOCs were estimated to increase from 148 to 253 Gg during the period of 2005–2014 (Zhao *et al.*, 2017). Under prevailing northeastern and southeastern winds, Nanjing is located downwind of the entire YRD region and is influenced by the long-distance transport of pollutants. Ding *et al.* (2013) and Chen *et al.* (2019) reported high levels of O₃ and PM_{2.5} concentrations with near-surface observation data in this region. In this study, we conducted simultaneous online measurements of ambient VOCs at suburban areas for a full year. The diurnal and seasonal variations in VOCs and diagnostic ratios were evaluated to understand the temporal differences of VOCs levels. The sources of VOCs were identified, and their contributions to ambient concentrations were quantified through the positive matrix factorization (PMF) method. Both the PMF method and the PCA/APCS models do not need prior information about the number of VOCs sources and the VOCs emission source profiles. However, PMF model was chosen over PCA/APCS models because it could identify VOCs sources by limiting all the elements in the factor profiles and the factor loading matrix to positive values (Yuan *et al.*, 2009), and could deal appropriately with data that are below the method detection limit (MDL; Hu *et al.*, 2018). Finally, the source contribution during O₃ and PM_{2.5} pollution days was investigated to improve policy making regarding air quality improvement.

METHODS

Site Description

VOCs measurements were conducted at the Xianlin Campus of Nanjing University (NJU; 32.12°N, 118.96°E) in Nanjing, as shown in Fig. 1. The instruments at NJU were set on the roof of a building, 20 m above the ground. NJU is a suburban site, located in northeastern Nanjing, approximately 20 km from downtown (Li *et al.*, 2016; Chen *et al.*, 2017). Under the prevailing southeastern winds in the summer monsoon season, NJU has often been affected by urban plumes from the megacity Shanghai and the Suzhou-Wuxi-Changzhou city cluster (Zhao *et al.*, 2019).

Due to the technical problems with the instruments at NJU, other species in the atmosphere, including O₃, PM_{2.5}, carbon monoxide (CO) and nitrogen dioxide (NO₂), were measured and reported at a state-operated air quality observation site in Xianlin (XL; 32.11°N, 118.91°E; <https://data.epmap.org>). The XL site is 4.5 km west of the NJU site, as shown in Fig. 1. Our previous study demonstrated that the relatively close distances did not lead to a large bias in air quality (Chen *et al.*, 2017); thus, we can assume that the data from the XL site is representative of the atmospheric conditions around NJU.

Sampling and Analysis

The concentrations of 55 VOCs species were measured by an online O₃ Precursor Analyzer System (PerkinElmer (PE), Waltham, MA, USA) from March 2016 to February 2017 at NJU. At a flow rate of 15 mL min⁻¹, air samples were collected for 40 min every hour and then passed through a Nafion dryer to remove water vapor. The dried samples were first concentrated in a trap maintained at -30°C and later desorbed when the trap was heated to 350°C at a rate of 40°C s⁻¹ in the thermal desorbers (TD 300; PE). Finally, the compounds were transferred into a gas chromatograph system (GC 580; PE) by an ultra-pure (99.999%) helium carrier.

The gas chromatograph system was operated with two columns and two flame ionization detectors (FIDs). 55 compounds, including alkanes, alkenes and aromatic hydrocarbons, were classified into C₂–C₆ and C₆–C₁₂ categories. The former was separated in the PLOT column (Al₂O₃/Na₂SO₄, 50 m × 0.32 mm × 5 μm) and then identified by the first FID. The latter was separated in the BP-1 column (Al₂O₃/Na₂SO₄, 50 m × 0.22 mm × 1 μm) and then identified by the second FID. The temperature program for the GC oven was increased from 46°C to 170°C at a rate of 5°C min⁻¹, then increased to 200°C at a rate of 15°C min⁻¹, and was finally maintained at 200°C for 9 min. The sample residence time for measuring VOCs with GC-FID was 50 min, and a chromatogram with identified retention times is presented in Fig. S1.

The analytical uncertainty on species was evaluated from the observed reproducibility and linearity of standard gas. Running for ten times, the relative standard deviations of concentration-response (peak area) were 0.34–2.78% for 55 species. The calibration curves were obtained by running the five diluted standards and the correlation coefficients for the calibration curves were 0.9929–0.9999 for 55 species. The

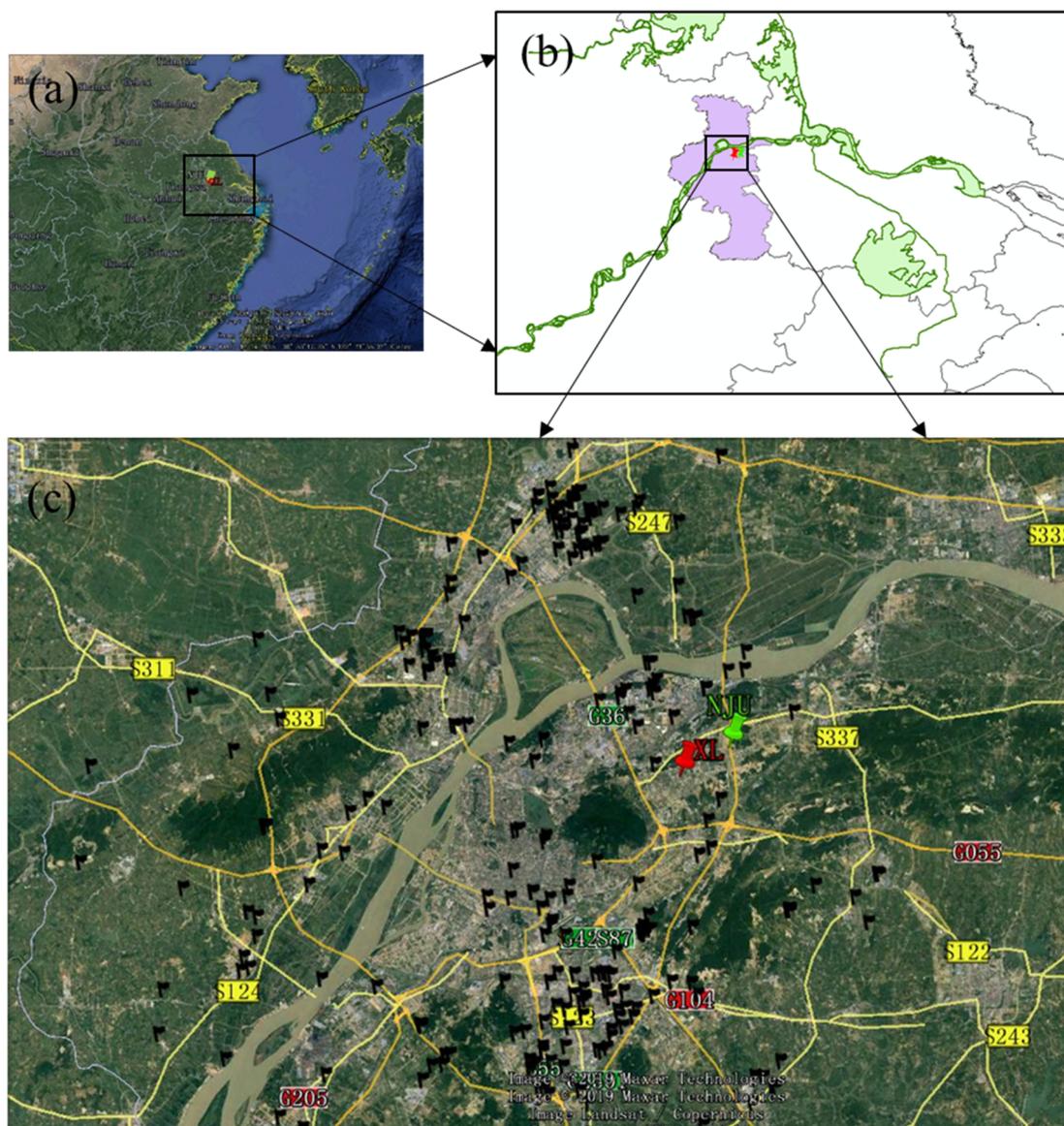


Fig. 1. The locations of the NJU and XL sites in Nanjing. The green and red marks represent NJU and XL site, respectively. The black flags are main factories with annual VOCs emission over 1 t. The (b) green lines and (c) yellow lines are river path and road, respectively.

analytical system was checked daily with a one-point calibration. The standard gases from the Photochemical Assessment Monitoring Stations (PAMS, Linde) were used at 00:00 every day. If the response was within $\pm 10\%$ of the initial calibration curve, the measurements were expected to be reliable. Fig. S1 illustrates the retention times of species in a sample and a standard gas, which were consistent with each other. The method detection limit (MDL) of a certain VOC was calculated according to Eq. (1) (Xia *et al.*, 2014):

$$MDL = \frac{3 \times N \times W}{H} \quad (1)$$

where N is the noise (mV), W is the concentration of the calibration sample (ppbv) and H is the response (mV). The MDLs of individual VOCs are listed in Table S1.

The methods recommended in the National Ambient Air Quality Standards in China (NAAQS-CN) were used for the measurement of other species at the XL site. O_3 and $PM_{2.5}$ were monitored with a Model 49i O_3 Analyzer and a Thermo Scientific TEOM 1405D, respectively, and the concentrations of NO_2 and CO were measured with Thermo Scientific TEOM 42i and 48i, respectively. All the samples were collected at hourly intervals. Meteorological data, including solar radiation, wind speed, air temperature, precipitation, relative humidity and surface air pressure, were recorded at the automatic weather station at NJU.

Positive Matrix Factorization (PMF)

The EPA PMF 5.0 program (U.S. EPA, 2014) was used to identify VOCs sources and to quantify their contributions. For a certain number of factors, PMF analysis can obtain the

factor contributions and factor profiles by minimizing the object function Q (Paatero and Tapper, 1994; Paatero, 1997):

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right)^2 \quad (2)$$

where i , j and k represent the VOCs compound, emission source and sampling, respectively; x represents the concentration; g represents the profile matrix; f represents the score matrix; and u represents the residual factor.

Both the concentration data file and the corresponding uncertainty data file are required as inputs of the PMF. For the concentrations, ND (not detected) data and data lower than the MDL were replaced by a value of half the MDL (Hopke et al., 2000; Yuan et al., 2012). Only species in which at least 70% of measurements were above the MDL were chosen for PMF analysis. Although the procedure in PMF model would eliminate “bad variables,” it categorizes a species as “bad” only if all the samples are missing (U.S. EPA, 2014; Ou et al., 2015). The uncertainties (*Unc*) of those concentration values (*Conc*) that were below or equal to the MDL were calculated using Eq. (3) (Polissar et al., 1998; Reff et al., 2007):

$$Unc = \sqrt{(Error\ Fraction \times Conc)^2 + (0.5 \times MDL)^2} \quad (3)$$

If the concentrations were higher than the MDL, Eq. (4) was used (Polissar et al., 1998; Reff et al., 2007):

$$Unc = \frac{5}{6} \times MDL \quad (4)$$

The *Error Fraction* in Eq. (3) was considered as measurement uncertainty and was set as 10% for all species.

PMF ran from four to ten factors to obtain meaningful solutions. The determination of PMF factor number was shown in Section S1.

Concentration-weighted Trajectory (CWT)

The CWT model, reflecting the concentration levels of the trajectories, was used to distinguish the pollution levels of different potential regions and to identify the potential source regions of atmospheric VOCs. The 48-h backward trajectories with 1-h intervals (from 01:00 to 23:00 local time (LT)) were simulated for each day from March 2016 to February 2017 with TrajStat (Wang et al., 2009). The details were shown in Section S2.

RESULTS AND DISCUSSION

Concentrations and Temporal Variations in Ambient VOCs

The annual mean concentrations, standard deviations (SD) and MDLs of all 55 VOCs species at NJU are summarized in Table S1. The mean concentration of the total VOCs was 18.9 ppbv, and alkanes, alkenes and aromatics contributed 67.5%, 13.6% and 18.9% of the total mass concentration, respectively. The top 10 abundant species were propane, ethane, *n*-butane, *i*-pentane, ethene, toluene, *i*-butane, benzene, *n*-pentane and propene, and their concentrations collectively accounted for 76.7% of the total VOCs concentrations. The top 10 abundant species and their average concentrations were compared with the results of previous studies conducted in the YRD region, as shown in Table 1. The top 10 abundant species at the industrial site in Nanjing (An et al., 2014) were similar to those in this study, with slight differences in their ranking, emphasizing the differences of dominant VOCs sources at two areas. Furthermore, the average concentrations of VOCs components observed in this work were generally lower than those in An et al. (2014), with the differences ranging from 0.16 to 4.47 ppbv. The measurement site reported in An et al. (2014) was 25 km from NJU and was located

Table 1. Comparison of the top ten abundant species and their average concentrations measured in different cities in the YRD region (unit: ppbv).

Nanjing ^a		Nanjing ^b		Ningbo ^c		Shanghai ^d		The mid-lower Yangtze River ^e	
Suburban		Industrial		Suburban		Urban		Waterway	
Propane	3.29	Ethane	6.97	Ethane	2.45	Propane	4.81	Ethane	7.44
Ethane	2.89	Ethene	5.68	Propane	2.37	Toluene	4.70	Propane	5.66
<i>n</i> -Butane	1.53	Propane	3.29	Ethene	1.92	<i>i</i> -Pentane	2.29	Ethene	5.24
<i>i</i> -Pentane	1.26	Benzene	3.14	<i>i</i> -Butane	1.72	<i>n</i> -Butane	2.03	<i>n</i> -Butane	4.36
Ethene	1.21	Propene	2.45	<i>n</i> -Butane	1.26	Benzene	1.81	Propene	3.78
Toluene	1.07	Toluene	2.10	Propene	1.05	<i>i</i> -Butane	1.43	<i>i</i> -Butane	1.72
<i>i</i> -Butane	0.98	<i>n</i> -Butane	1.69	Toluene	0.90	<i>m,p</i> -Xylene	1.40	<i>i</i> -Pentane	1.50
Benzene	0.82	1-Butene	1.61	<i>i</i> -Pentane	0.75	Ethylbenzene	1.23	Toluene	1.09
<i>n</i> -Pentane	0.78	<i>i</i> -Butane	1.51	Benzene	0.45	Propene	0.84	<i>n</i> -Pentane	1.04
Propene	0.70	Ethylbenzene	1.19	<i>m,p</i> -Xylene	0.40	-	-	-	-

^a This study. Sampling period: from March 2016 to February 2017.

^b An et al. (2014). Sampling period: from March 2011 to February 2012.

^c Mo et al. (2017). Sampling period: December 2012, April 2013, July 2013, and October 2013.

^d Cai et al. (2010). Sampling period: from January 2007 to March 2010.

^e Zhu et al. (2018). Sampling period: from November 2015 to December 2015.

approximately 3 km from a large-scale industrial chemical park; as such, the strong emissions from those sources would have a greater influence on the ambient VOCs levels. The annual average concentration of species in suburban Nanjing was similar to that in Ningbo (Mo *et al.*, 2017) but lower than that in Shanghai (Cai *et al.*, 2010). This result was reasonable, since the VOCs emissions were usually higher in Shanghai than in Nanjing and Ningbo (Huang *et al.*, 2011). The most significant species in this study differed from those in urban Shanghai. Nanjing had high abundances of C₂–C₄ alkanes, while Shanghai was rich in aromatics. The differences in dominant species probably highlighted the various sources of VOCs. In addition, the concentrations of VOCs species along the mid-lower Yangtze River were higher than those in this study, which might be attributed to the influence of ship emission along the waterway. The TVOCs and chemical groups between this study and previous studies observed at other metropolitan areas in the world were also compared, as shown in Table S2. The annual average concentration of TVOCs in this study was similar to that in suburban Yokohama (Tiwari *et al.*, 2010) but lower than Guangzhou (Zou *et al.*, 2015). It was lower than that in urban areas in other cities such as Beijing (Wang *et al.*, 2010), Wuhan (Hui *et al.*, 2018), Chung-Ming (Huang *et al.*, 2019),

Paris (Baudic *et al.*, 2016), Mexico City (Garzon *et al.*, 2015) and Houston (Leuchner and Rappengluck, 2010).

The seasonal variations of TVOCs, chemical groups and selected VOCs species observed at NJU are shown in Fig. 2. These species, including the top 10 abundant species, ethylbenzene and *m,p*-xylene, were typical tracers for various VOCs sources. For example, C₂–C₅ alkanes could be emitted from vehicle exhaust or fuel evaporation, while aromatics were tracers of solvent usage. Similar seasonal patterns were found for most VOCs species and chemical groups, i.e., the highest concentrations were observed in winter, and the lowest concentrations were observed in summer. The mean concentrations of those VOCs species in winter were 28–158% higher than those in summer. The higher concentrations in winter resulted from diminished photochemical activities under suppressed diffusion conditions and lower temperature, while the lower concentrations in summer could result from intensive photochemical reactions in the atmosphere. The concentrations of some species, such as butane isomers and pentane isomers, were observed to increase slightly in summer. These species are tracers of engine exhaust or fuel evaporation. George *et al.* (2015) found that vehicle emissions measured in warm ambient temperatures were lower than those in cold temperatures.

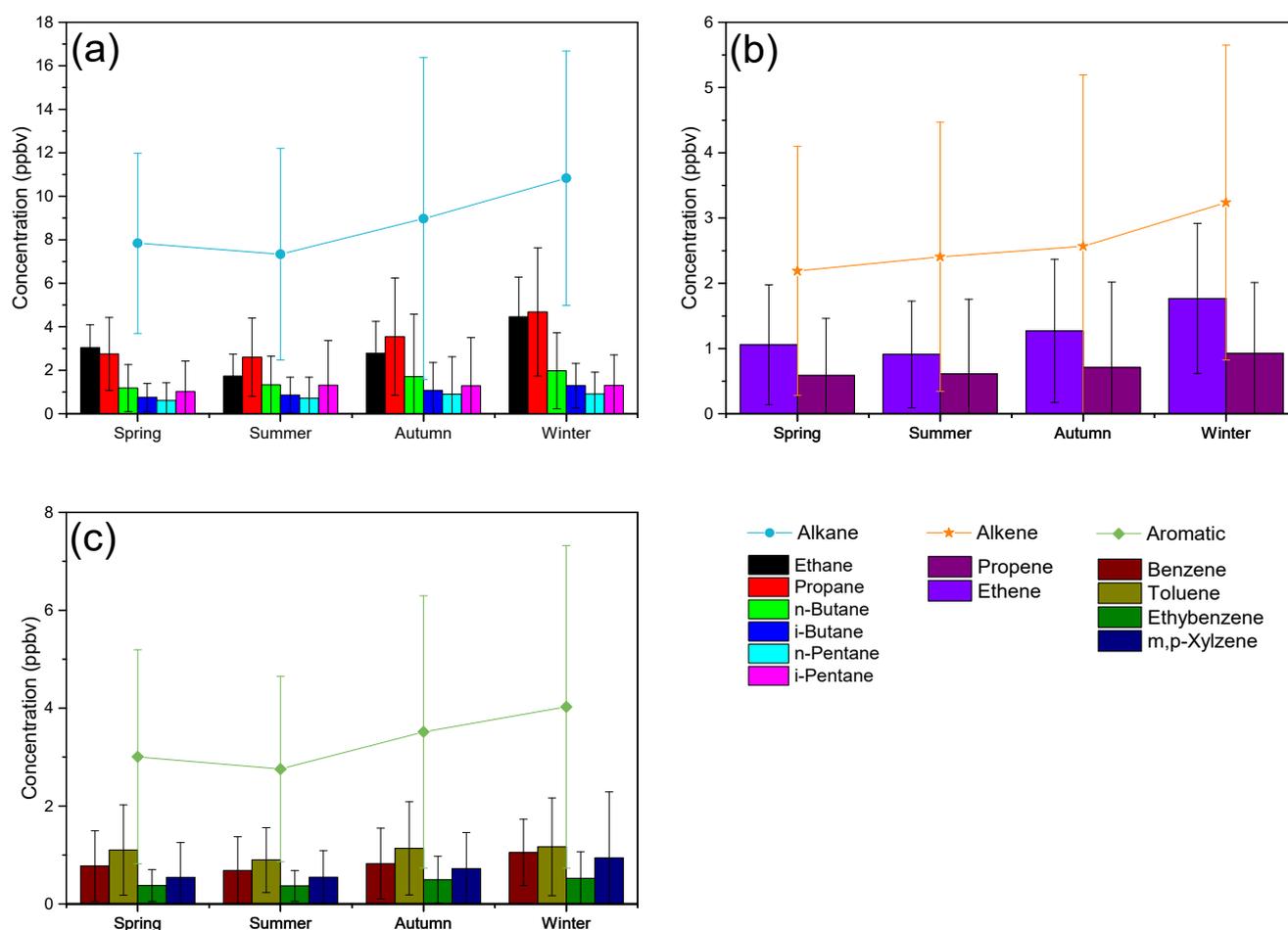


Fig. 2. Seasonal variations in (a) alkanes, (b) alkenes and (c) aromatics during the sampling period. The error bars represent ± 1 standard deviation from the total averages.

Therefore, the results emphasized the volatilization of VOCs from evaporation in suburban areas. For chemical groups, the concentration of alkenes was observed to slightly increase in summer, suggesting the presence of additional sources, e.g., biogenic sources with substantial isoprene emissions (Mochizuki *et al.*, 2014).

Fig. 3 shows the diurnal variations of TVOCs, chemical groups and selected VOCs species. The VOCs exhibited similar trends, with concentrations accumulating at night and decreasing during the day. Despite the continuous release of VOCs, the VOCs levels were reduced because of the oxidation of VOCs by OH radicals during the day and the increased dispersion and dilution of pollutants due to the elevation of the planetary boundary layer (PBL).

The Concentration Ratios of Selected Species by Season

The chemical compositions of VOCs in the emission sources were assumed to be relatively constant throughout the day, and it was assumed that the abundance of the more reactive species in the atmosphere would decrease during the day due to photochemical reactions. Therefore, the VOCs ratios for ambient concentrations have often been used to explore the emission sources of VOCs and the photochemical age of air masses (Yan *et al.*, 2017; Zheng *et al.*, 2018). In this study, the ratios of *i*-pentane to *n*-pentane (I/N) and of *m,p*-xylene to ethylbenzene (X/E) were selected. The correlations of the two pairs of species at the seasonal level are illustrated in Fig. 4.

The pentane isomers had approximately the same rate of reaction with OH radicals (Atkinson, 1986), and their ratio was a reliable indicator for the identification of emission sources, since these compounds were equally affected by photochemical processing. A higher ratio of I/N was reported in vehicle emissions (2.2–3.8) and fuel evaporation (1.8–4.6) than in NG evaporation (0.82–0.89) (Gilman *et al.*, 2013; McGaughey *et al.*, 2004; Watson *et al.*, 2001). In this study, the squared correlation coefficient values (R^2) of the linear regression fitting for the pentane isomer ratios were large (0.65–0.91), indicating a similar source for the two species. The ratios of I/N ranged from 1.2–1.9 according to season at NJU, with the maximum values found in summer. Since the effects of photochemical processing on pentane isomers were equal, the higher I/N ratio in summer probably indicated that the larger influence of fuel evaporation (not vehicle emissions since the emission strength of vehicles would be stronger in cold weather). The ratios at NJU suggested that the pentanes were more likely from the mixed sources of NG and fuel evaporation. This assumption was proved by the correlation analysis between pentane isomers and other VOCs species. As shown in Table 2, the pentane isomers at the NJU site displayed stronger correlations ($0.72 < R^2 < 0.85$) with butane isomers (typical tracers of gasoline) and weaker correlations ($0.11 < R^2 < 0.41$) with alkenes and aromatic hydrocarbons (associated with vehicle exhaust). This result suggested that gasoline evaporation contributed a greater concentration of pentane isomers in suburban areas.

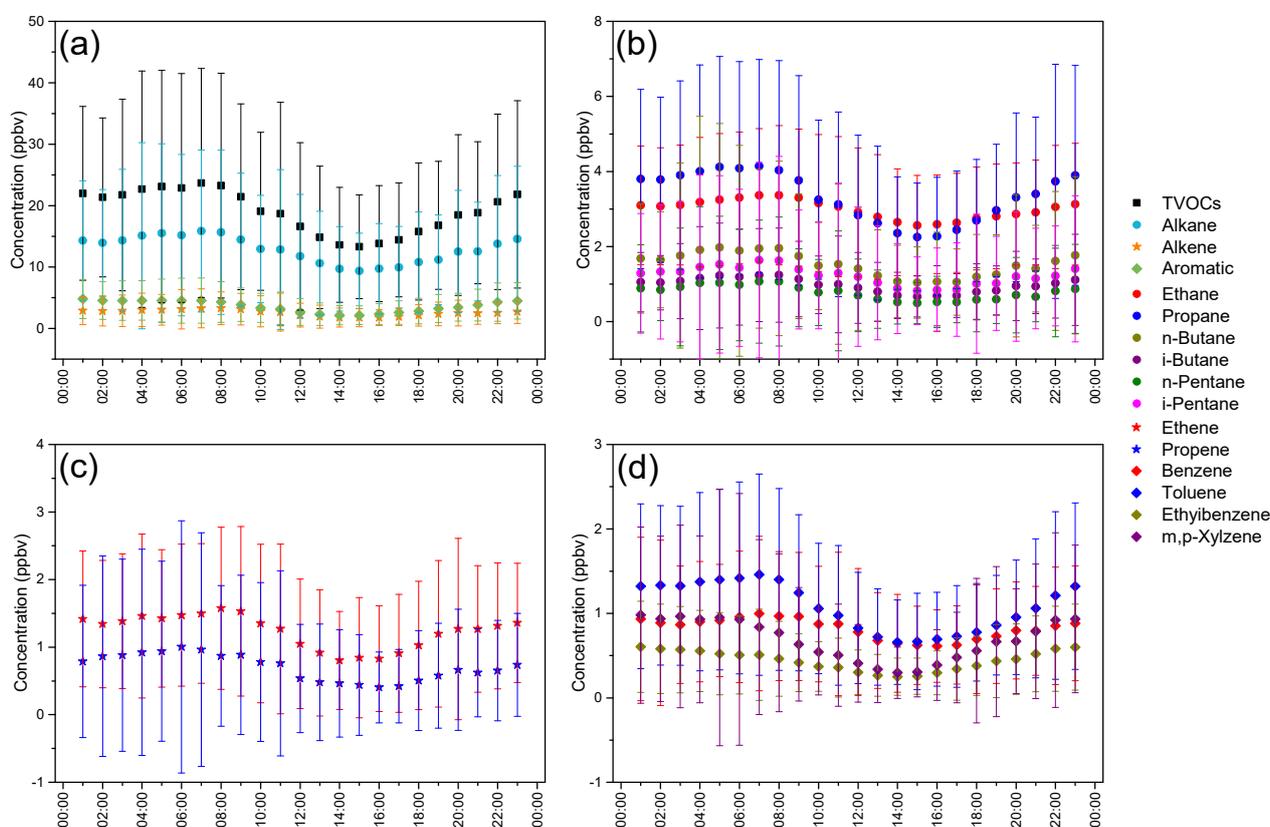


Fig. 3. Daily variations in (a) TVOCs and chemical groups, and (c–d) twelve species during the sampling period. The error bars represent ± 1 standard deviation from the total averages.

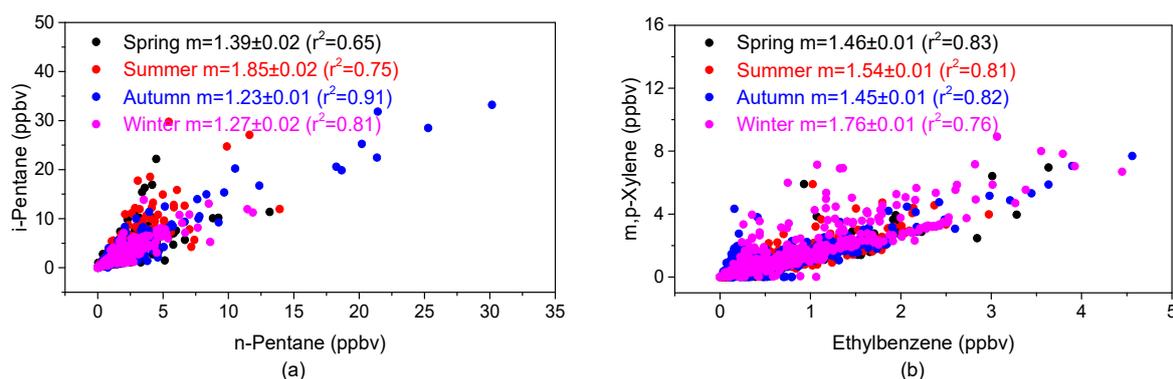


Fig. 4. Correlations between (a) *i*-pentane and *n*-pentane and between (b) *m,p*-xylene and ethylbenzene. Linear regression fitting is applied to symbols in each season and the corresponding slopes ($m = \text{slope} \pm \text{standard error}$) and correlation coefficients (R^2) are shown in the plots.

Table 2. Correlations (R^2) between species at the NJU site.

	<i>n</i> -Pentane	<i>i</i> -Pentane
Ethane	0.23	0.19
Propane	0.41	0.32
<i>n</i> -Butane	0.85	0.72
<i>i</i> -Butane	0.74	0.75
Ethene	0.22	0.17
Propene	0.31	0.26
Benzene	0.26	0.20
Toluene	0.14	0.11

The ratio of *m,p*-xylene to ethylbenzene (X/E) was a typical indicator of photochemical age. The atmospheric lifetime of ethylbenzene (1.6 days) was longer than that of *m,p*-xylene (11.8–19.4 h; Monod *et al.*, 2001), and the ratio of X/E decreased as the VOCs air masses underwent photochemical reactions in the atmosphere. An X/E ratio below 3 was identified as “aged” due to long-range transport, whereas a ratio above 3 was considered a local emission (Kuntasal *et al.*, 2013; Yurdakul *et al.*, 2018). As shown in Fig. 4(b), the ratios at NJU were estimated to be 1.5–1.8, showing that the air masses that affected the observation points exhibited a certain degree of aging. The highest ratios occurred in winter as expected due to weak photochemical activities. The diurnal variations of X/E are shown in Fig. S2. It was observed to continuously decline by 35% from 07:00 to 15:00 LT, indicating the increased photochemical removal processes during the day.

Source Apportionments and Geographic Origins of VOCs

Source contributions to VOCs were calculated using the PMF model for hourly samples throughout the entire year. Only 24 species including 13 alkanes, 3 alkenes and 8 aromatics were used in the PMF model, since 70% of their concentrations were above the MDL. According to the variations of Q/Q_{exp} and factor profiles, introduced in Section S1, a seven-factor solution was finally chosen. The R^2 value between the calculated and measured total VOCs concentrations at NJU was 0.98, showing that the PMF solutions could well explain the variance in the total measured concentrations. Fig. 5 illustrates seven source profiles and

their contributions to the annual ambient VOCs extracted from the PMF, and the seasonal and diurnal variations of the factor contributions are provided in Fig. 6 and Fig. S3, respectively.

Factor 1 consisted mainly of toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, *m*-ethyltoluene, 1,2,4-trimethylbenzene, and methylcyclopentane, and was consistent with the source profiles of solvent usage measured in Wang *et al.* (2014). Although aromatics were also reported to be emitted from traffic emissions (Borbon *et al.*, 2001; Buzcu *et al.*, 2006), Factor 1 was regarded as solvent and painting since it had higher contributions in summer (15%) than winter (11%) (Fig. 6). Previous studies have demonstrated that emission strength of vehicular exhaust would be higher at cold temperature while that of solvent usage would be higher at warm temperature (George *et al.*, 2015; Song *et al.*, 2019).

The main tracer species of Factor 2 were methylcyclopentane, benzene, cyclohexane, *n*-heptane and toluene. These species have been reported to be emitted from petroleum refineries (Bari and Kindzierski, 2018). The average contributions of this factor were rather stable in both day and night. The seasonal variation in this factor displayed higher contributions in spring–summer (14%) than in autumn–winter (6–12%), consistent with the emission strength of petrochemical plants. The petrochemical plants would contribute more VOCs at higher temperatures (Song *et al.*, 2019). Therefore, Factor 2 at NJU was expected to represent petrochemical plants.

Large fractions of ethane (59%) were found in Factor 3. Ethane is the main species of natural gas (NG; Xiao *et al.*, 2008; McCarthy *et al.*, 2013), and it has a long atmospheric lifetime (Zheng *et al.*, 2018). As shown in Fig. S3(c), the contributions of Factor 3 were larger in the afternoon, when the ambient levels of oxidation products were usually high. Therefore, Factor 3 was likely a mixture of NG and aged air masses. Besides, the seasonally averaged contributions of this factor significantly varied, from 12% in summer to 21–28% in winter–spring. It further proved that concentrations of this factor likely resulted from aged air masses, since weaker photochemical reactions and atmospheric dynamics in winter would lead to greater accumulation of VOCs, and thus, to higher source contributions.

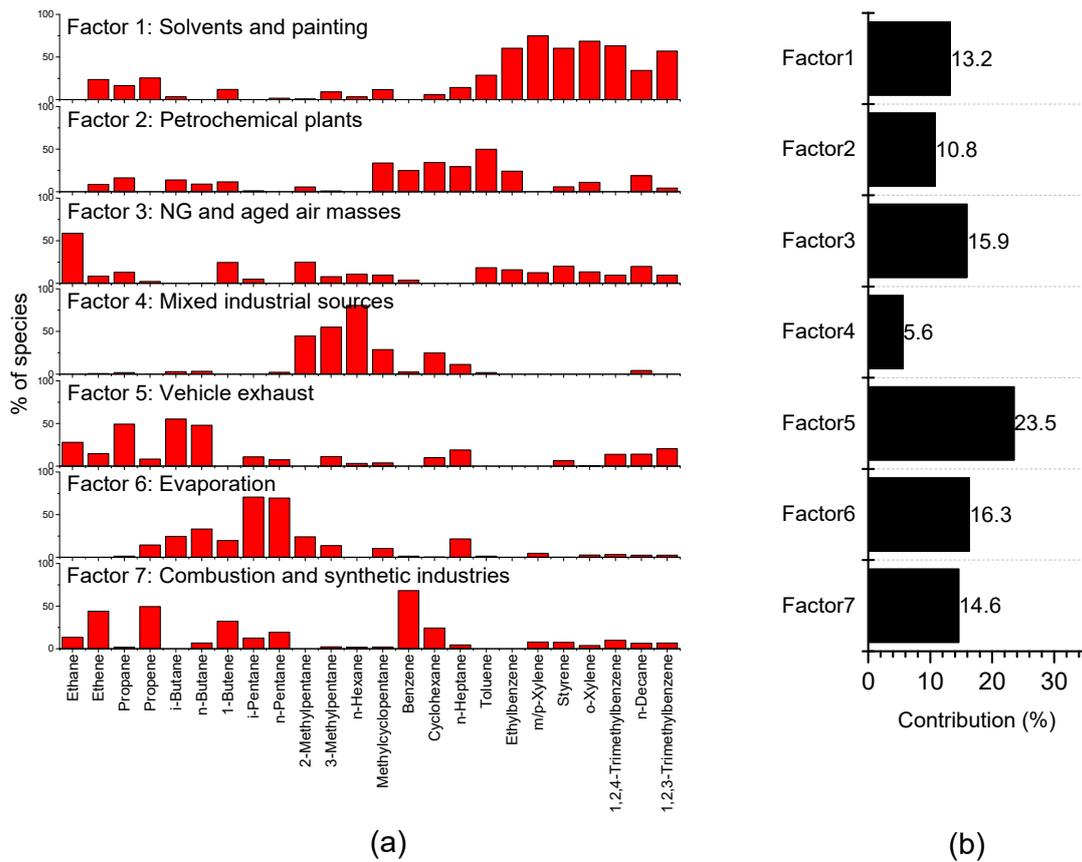


Fig. 5. (a) The identified sources with VOCs profiles and (b) their contributions to annual VOCs from the PMF model at the NJU site.

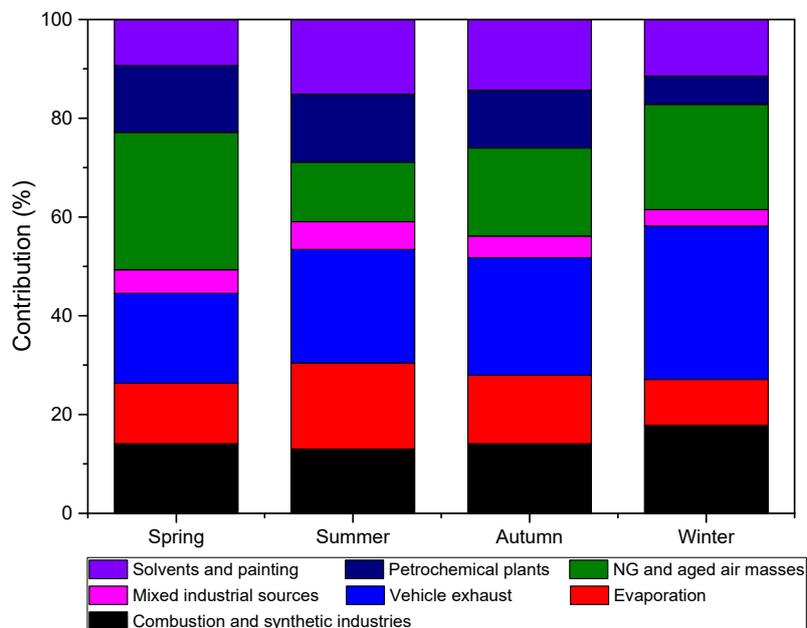


Fig. 6. Variations in the seasonal averaged contributions of the seven modeled VOCs sources (expressed in percent).

n-Hexane and its isomers 2-methylpentane and 3-methylpentane had high percentage contributions in Factor 4. *n*-Hexane is an ingredient of special glues that are used in the shoe-making and leather industries. It has also been

reported that *n*-hexane is used as a cleansing agent for shoes, furniture and textiles (ATSDR, 1999). 2-Methylpentane has been widely used as a nonpolar solvent (Kwon *et al.*, 2007). As shown in Fig. S3(d), the diurnal variation of this factor

was characterized by a double-wave profile, with an initial increase from 09:00 to 12:00 LT and a second increase between 14:00 and 18:00 LT, consistent with the daily working hours. Therefore, Factor 4 was identified as mixed industrial sources associated with private shops that serve the daily needs of the nearby population.

The species in Factor 5 and Factor 6 appeared to overlap. High loadings of propane, *i*-butane and *n*-butane were found in Factor 5, similar to the source profile of LPG taxis investigated in Hong Kong (Ho *et al.*, 2013). For Factor 6, pentane isomers and butane isomers were weighted relatively more. C₃–C₅ alkanes were the main components of LPG, NG and gasoline (McCarthy *et al.*, 2013; Barletta *et al.*, 2005). To further distinguish these two factors, correlation analysis was conducted between factor contribution and relevant vehicle exhaust markers (NO₂ and ethene; Brown *et al.*, 2007; Bari *et al.*, 2018), as shown in Fig. S4(a)–S4(d). Factor 5 displayed moderate correlations with NO₂ ($R^2 = 0.26$) and ethene ($R^2 = 0.39$), while Factor 6 displayed poor correlations with NO₂ ($R^2 = 0.04$) and ethene ($R^2 = 0.12$). On the other hand, the highest contribution of Factor 5 was observed in winter (31%), whereas the highest contribution of Factor 6 was observed in summer (17%). These seasonal variations were consistent with the emission strength of vehicle exhaust and fuel evaporation, respectively. Therefore, Factor 5 could be identified as vehicle exhaust and Factor 6 could be identified as fuel evaporation.

Factor 7 was dominated by ethene, propene and benzene, and was moderately influenced by C₄ alkene. These species are the key markers of combustion. Ethene and propene are also used as feedstock in synthetic industries. As shown in Fig. S4(e), Factor 7 displayed moderate correlations with CO ($R^2 = 0.30$), a tracer for combustion sources (Borbon *et al.*, 2013; Barletta *et al.*, 2016). Therefore, Factor 7 was supposed to be a mixed source of combustion and synthetics. As shown in Fig. S3(g), the contributions of Factor 7 were clearly elevated during the day (from 08:00 to 17:00); thus, this factor was attributed to industrial sources related to combustion and chemical synthesis engineering.

In summary, traffic emissions (i.e., vehicle exhaust), and NG and aged air masses contributed 23.5% and 15.9% of VOCs in suburban areas. The emissions from solvents and painting (13.2%), petrochemical plants (10.8%), mixed industrial sources (5.6%), evaporation (16.3%) and combustion and synthetic industries (14.6%) were grouped as “industrial emissions,” and they were estimated to collectively contribute 60.5% to the ambient VOCs. However, according to a local emission inventory by Zhao *et al.* (2017), the main contributor of anthropogenic VOCs in Nanjing was industrial emissions (81.8%), including industrial processes (49.9%) and solvent usage (30.9%), which were significantly larger than those from traffic emissions (9.7%). A larger contribution of traffic emissions from the receptor model has often been found in previous studies (Yuan *et al.*, 2013; Sarkar *et al.*, 2017; Song *et al.*, 2019). For example, in a study conducted in Seoul (Song *et al.*, 2019), the mean contributions of traffic emissions were 44% as determined by PMF and 14% as determined by the national emission inventory. The PMF factors probably represented groups of sources rather than specific emission

sources. In this study, for example, species in Factor 5 (vehicle exhaust) might also be influenced by the petrochemical industry. Furthermore, the measured VOCs ratios did not exactly represent the emission ratios due to chemical reactions in the atmosphere. The source apportionment result might overestimate the contribution from traffic since unreactive species, such as C₂–C₅ alkanes, are more abundant in the emissions. In contrast, the contribution of solvents and painting sources might be underestimated, as they emitted species with relatively short atmospheric lifetimes (e.g., toluene, *m,p*-xylene, and *o*-xylene). The uncertainties in the emission inventory could also partly explain the discrepancies. For example, the vehicle population in Nanjing increased by 16% from 2014 to 2016 (Bureau of Statistics of Nanjing, 2015, 2017), and elevated emissions of transportation could be expected in recent years.

Nonetheless, the contribution of traffic emissions to the ambient VOCs level in this study was comparable to those estimated for other selected Chinese cities by receptor models. The contribution at NJU, for example, was slightly smaller than the reported result for an urban site in Wuhan (28%; Lyu *et al.*, 2016) and much smaller than the reported results in Beijing (44%; Gao *et al.*, 2018) and Hong Kong (48%; Guo *et al.*, 2011). The discrepancies between cities could be attributed to the different patterns of economic development and the different degrees of progress of emission control for vehicles.

The CWT provided insights into the potential geographic origins of VOCs sources, as shown in Fig. 7. The highest areas of pollution were found to the northwest of NJU, where industrial plants are densely located. The result thus suggested that the VOCs levels at NJU were strongly influenced by local industrial sources. Furthermore, the CWT results revealed that air masses from the northeastern YRD made a large contribution. As mentioned above, surface wind in Nanjing originated mostly from the northeast in winter and from the east and southeast in summer (Ding *et al.*, 2013); thus, surface winds brought polluted air from the YRD and influenced the air quality downwind of Nanjing.

Source Contributions for Clear and Pollution Days

Based on high-temporal resolution datasets, the source apportionment also provided a unique opportunity to explore the possible variation in source contributions to the inferior air quality during pollution events. The information about the O₃ and PM_{2.5} mass concentrations at the XL site was used to define the pollution events according to the NAAQS-CN. Here, we defined O₃ pollution days as the days with 1-h average O₃ mass concentrations exceeding the Class II NAAQS (200 μg m⁻³) for 4 collective hours. The days with daily average PM_{2.5} mass concentrations exceeding the Class II NAAQS (75 μg m⁻³) were defined as PM_{2.5} pollution days. The days with an air quality index (AQI) lower than 50 were defined as clear days. The calculation of the AQI is provided by the China National Environmental Monitoring Center (<http://www.cnemc.cn/>) and is introduced briefly in Section S3.

The selected dates and related air quality data are shown in Fig. S5. There were 19 days of O₃ pollution, and most of

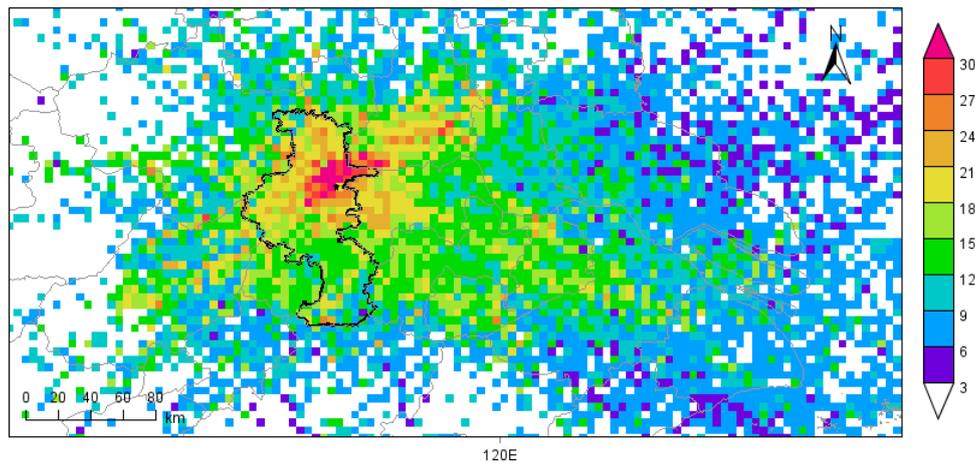


Fig. 7. Geographic origins of the VOCs sources (shaded with colors) identified by concentration weighted trajectory analysis at the NJU site. The black star represents the sampling site.

these days were during warm seasons (May and July–September). O_3 pollution in suburban areas occurred early in May, which is possibly attributed to the large amount of precursor emissions from broader regions in the YRD. Xie *et al.* (2016) indicated that the peak O_3 in spring could be first attributed to regional contributions and then to local contributions, whereas an opposite trend was observed in summer. In total, 31 $PM_{2.5}$ pollution days were observed, and most of these days were in winter and early spring because of the frequent unfavorable conditions of atmospheric diffusion. 17 clear days were observed.

The source contributions to ambient VOCs on clear and pollution days are summarized in Table S3, and Fig. 8 illustrates the absolute contribution ratios in different kinds of days (a) and the relative changes in pollution days compared to clear days (b). During the $PM_{2.5}$ pollution days, the contributions of solvents and painting, petrochemical plants, NG and aged air masses, vehicle exhaust, and combustion and synthetic industries were elevated by 17.9%, 16.8%,

14.4%, 12.3%, and 4.5%, respectively. Accordingly, the contributions of mixed industrial sources and evaporation were reduced by 36.8% and 36.7%. Aromatic hydrocarbons emitted from solvents and painting and from petrochemical plants had relatively high SOA formation potential. Therefore, the contributions of these sources were observed to increase when $PM_{2.5}$ levels increased. Furthermore, $PM_{2.5}$ pollution episodes often occurred under the unfavorable condition of atmospheric diffusion that increased the residence time of air and thus, the contributions of aged air masses were enhanced. Unlike $PM_{2.5}$ pollution events, the contributions of vehicle exhaust and of combustion and synthetic industry decreased by 1.4% and 19.5%, respectively, during O_3 pollution episodes, along with a dramatic increase in the contributions of petrochemical plants (56.4%) and solvents and painting (22.6%). Except for the high O_3 formation potential of species from petrochemical plants, these sources contributed more VOCs in the spring–summer (Fig. 6) because of higher temperatures, therefore leading to

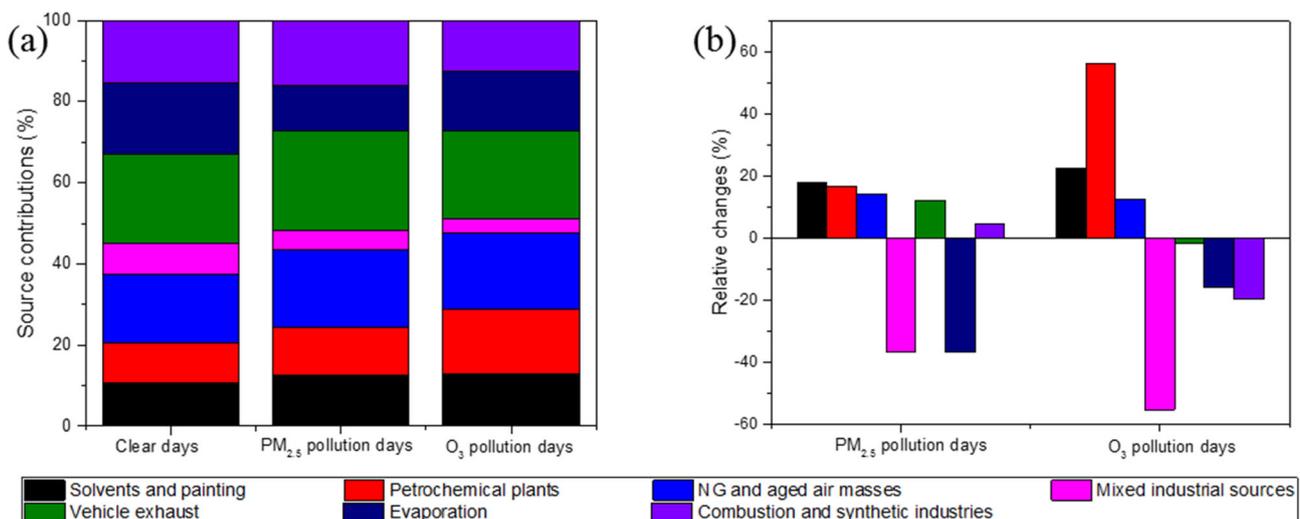


Fig. 8. (a) Source contributions for pollution and clear days and (b) relative changes in the source categories on pollution days compared to those on clear days at the NJU site.

a rise of O₃ levels. The larger contribution of aged air masses during O₃ pollution days indicated the importance of regional transport in suburban areas. The results of the contributions of VOCs sources on pollution days suggested that reducing industry-related (especially petrochemical industry and solvents and painting) emissions is an effective way to improve air quality. The regional transport of aged air masses should also be taken into account in order to reduce VOCs levels in suburban areas.

CONCLUSIONS

The concentrations of 55 VOCs species were measured based on hourly observations at a suburban site from March 2016 to February 2017 in Nanjing, China. It was found that the VOCs were dominated by alkanes, followed by aromatics and alkenes, and their concentrations and compositions differed from those in industrial areas in Nanjing. Furthermore, autumn and winter exhibited higher concentrations than spring and summer for most of the species. The ratios for *i*-pentane/*n*-pentane and *m,p*-xylene/ethylbenzene indicated that the atmospheric VOCs in suburban Nanjing were influenced by fuel evaporation and long-distance transport. Source apportionment, as determined by PMF, revealed that large local emissions, particularly vehicle exhaust and evaporation, were key factors in the high levels of ambient VOCs. Additionally, the contribution from traffic exceeded that in the local emission inventory due to uncertainties in both methodologies. The CWT results demonstrated that the VOCs in this study mainly originated in the industrial areas of northeastern Nanjing and the upwind YRD. In light of the various contributions to VOCs during pollution episodes, reducing industrial emissions, especially from petrochemical industries, and solvents and painting, may be an effective way to improve air quality. Moreover, the significant contribution of regional aged air masses in suburban areas emphasizes the importance of jointly controlling VOCs on a broader regional scale.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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